Benzene and Toluene Removal by *Pandanus amaryllifolius Roxb* (Pandan Leaves): Effect of Pretreatment and Drying

by

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Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2005

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CERTIFICATION OF APPROVAL

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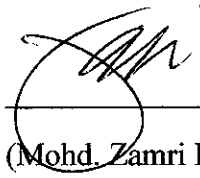
Approved by,



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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and the original work contained herein have not been undertaken or done by unspecified sources of person.

MARINA BT MOSIR

ABSTRACT

Benzene and toluene is typical toxic organic compound that appear very often in chemical and petrochemical wastewaters. These chemicals are classified as carcinogenic and mutagenic. Their presence in the environment, usually in wastewater at low concentration, is a major concern. Various methods could be used in removing these contaminants which include the fixed bed adsorption method. This study requires the student to do researches on the method using *Pandanus amaryllifolius Roxb* leaves as the adsorbent to remove organic compounds. This leaves is believed to be feasible in the removal of the compounds due to its carbon network of the cell wall. The objective of this research is to see the efficiency of the adsorption process using this leaves. Besides, to observe the rate of adsorption using the biomass, few pretreatments and drying methods were applied. Thus, various pretreatment using acids and base are being performed to study the effect of the pretreatment towards the uptake of the benzene and toluene. Also, moisture content in the biomass of the fixed bed adsorption column are analyzed and removed for a much efficient adsorption process. The study was done in a series of experiments. Samples obtained were analyzed using the Ultraviolet-Visible Spectrophotometer (UV-Vis) and Gas Chromatography Mass Spectrometer (GCMS). Results obtained shows that removals of both benzene and toluene are able to be accomplished through the process of fixed bed adsorption using *Pandanus amaryllifolius Roxb* leaves as adsorbent. Optimum conditions for adsorption to happen were obtained in this project. Over time, it is observed that these organic compounds decreases as it came in contact with the biomass. In conclusion, *Pandanus amaryllifolius Roxb* leaves do adsorb both organic compounds and shows different rate of adsorption after being pretreated and dried.

ACKNOWLEDGEMENT

First and foremost, I would like to thank Allah S.W.T upon my completion of this Final Year Research Project course. I am most grateful to my supervisor Mr. Mohd Zamri Abdullah who gives a full commitment, continuous support and an utmost guidance throughout the project's period. Also to the Final Year Research Project Coordinators, Puan Nor Yuliana Yuhana and Mr. Bawadi Abdullah, for their support and assistance along the way. My deepest gratitude to Dr Hilmi Mukhtar, the Programme Head of Chemical Engineering Programme for the opportunity provided in completing this research project.

My thanks to all the Chemicals Engineering Programme's lecturers for their guidance and knowledge that had helped me to complete this project. My appreciation to Mr. Zaaba, Mr. Fauzi, Mr. Jailani, Mr. Jamalkhir, Mr. Mahadhir, Mr. Sahar and all the technicians of Chemical Engineering Programme for their full assistance throughout the way.

Last but not least, I would like to thanks all my friends who had helped me during the period. My thanks also go to my parents for their continuous support and encouragement in my completion of this project.

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CHAPTER 1
INTRODUCTION

1.1 Background of study

In environmental systems, one is keenly interested in the transfer of a chemical (contaminant) from one phase (or medium) to another and in the manner it distributes itself between phases at equilibrium. In most cases, contaminants are transported through mobile water or atmosphere into other natural biotic or abiotic phases or media. Depending on the material properties of individual phases and on variable environmental factors, the manner by which a contaminant is retained by individual natural phases can vary widely. For most organic contaminants, particularly electrically neutral species, the way a contaminant is retained by a biotic or abiotic matter falls mainly into either or both of the two categories; the contaminant adheres only onto the surface of a natural material, or it dissolves into the latter's molecular network. Although these different modes of action are not readily distinguishable to our eyes, they are consequential to the extent of contaminant uptake and to the activity and fate of the contaminant in its local environment. It is surely one of the concerns highlighted in the pollutions of the environment (Chiou, 2002).

In general, organic compounds are normally composed of a combination of carbon, hydrogen, and oxygen, together with nitrogen in some cases. These priority pollutants have been and are continuing to be selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity. As the techniques used to identify these specific compounds continue to improve, a number of newly methods of treating these effluents also have been upgraded and studied (Metcalf & Eddy, 2004).

Several methods of treatment in wastewater specifically have been set on operations widely. Adsorption process is also known as one of the treatment method which are clarified as an advanced wastewater treatment. Advanced wastewater treatment is defined as the additional treatment needed to remove suspended, colloidal and dissolved constituents remaining after conventional secondary treatment such as coagulation, flocculation and sedimentation.

Adsorption processes are process where one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent as separation is accomplished. In commercial processes, the adsorbent is usually in the form of small particles in a fixed bed. The fluid is passed through the bed and the solid particles adsorb components from the fluid. When the bed is saturated, the flow in this bed is stopped and the bed is regenerated thermally or by other method, for desorption to occur. The adsorbed material (adsorbate) is thus recovered and the solid adsorbent is ready for another cycle of adsorption.

Applications of liquid-phase adsorption include removal of organic compounds such as the benzene and toluene from wastewater or organic solutions, colored impurities from organics, and various fermentation products from fermentation effluents. Separations include aromatics from non-aromatics and fructose from glucose using zeolites (Geankoplis, 1993).

The principal types of adsorbents include activated carbon, synthetic polymeric, and silica based adsorbents, although synthetic polymeric and silica- based adsorbents are seldom used for wastewater adsorption because of their high cost (Metcalf & Eddy, 2004).

Activated carbon as discussed above is a microcrystalline material made by thermal decomposition of wood, vegetable shells and coal that has surface areas of 300 to 1200 m^2/g with average pore diameters of 10 to 60 Å. Organics compound are generally adsorbed by activated carbon. *Pandanus amaryllifolius Roxb* is one of those materials

that are feasible to act as activated carbons for the separations of certain compound to happen due to its characteristic and its carbon network of the cell wall (Geankoplis, 1993).

1.2 Problem Statement

Chemical and petrochemical industries involve the handlings of petroleum and chemical compounds, reactions of conversions of certain hydrocarbons and separations to occur. From these activities, it is found that the effluent coming out of this area is highly contaminated. Most of the hazardous organic compounds are often present in the wastewater. Benzene and toluene is typical toxic organic compound that appear very often in chemical and petrochemical wastewaters. These chemicals are classified as carcinogenic, mutagenic, teratogenic and high acute toxicity which could cause cancer or other long term effect diseases. Their presence in the environment, usually in wastewater at low concentration, is a major concern.

This project requires the student to study the removal of these hazardous compounds by using *Pandanus amaryllifolius Roxb* which is believed to be feasible for organic compound removal due to its carbon network of the cell wall. It is to see the efficiency of the method by using the fixed bed adsorption to the eliminations of benzene and toluene. It could improve the wastewater characteristics as to be discharges to the environment.

Besides that, adsorption process needs certain pretreatments for it to operate more efficiently. Thus, various pretreatment using acids, base or other solution needs to be performed to study the effect of the pretreatment towards the uptake of the benzene and toluene. Also, moisture content in the biomass of the fixed bed adsorption column could not be excluded from the process. A study of various drying techniques is to be performed to observe the effect of moisture contents towards the removal the organic compounds. These studies are made to see how the process of removing benzene and

toluene by using *Pandanus amaryllifolius Roxb* could be improved and operates more efficiently.

1.3 Objective and Scope of Study

1.3.1 Objective

The objective of the study is to study the effect of pretreatment and drying towards the removal of benzene and toluene from the wastewater.

1.3.2 Scope of Study

Study undergoes here is focusing on the fixed bed adsorption process done by using the *Pandanus amaryllifolius Roxb* leaves as an adsorbent and see its efficiency of removing benzene and toluene from wastewater solution. Also, it is to see the effect of pretreatment and drying techniques in obtained a much accurate adsorption process. The percent of removal between each different technique are to be compared and analyzed to get an optimum condition for an optimum adsorption to happen. Through out the project, experimental work is performed in observing and analyzing the theoretical part of the projects. Recommendations of new methods and procedures in upgrading the research are to be discussed.

CHAPTER 2
LITERATURE REVIEW

2.1 Organic Compounds

Organic compounds are determined to assess the presence of priority pollutants identified by the U.S. Environmental Protection Agency (U.S. EPA). These priority pollutants were selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity. Many of the organic pollutants are also classified as volatile organic compounds (VOCs). These volatile organic compounds which have a potential for carcinogenesis in humans are found in ground and surface waters (Metcalf & Eddy, 2004).

Much of the recent concern over drinking water quality has been directed toward organic contamination in drinking water. This concern involves not only source water contamination but the formation of disinfection by-products resulting from the interaction of disinfectants and precursors in the source water. Organic compounds has been thought to primarily affect surface waters, which have become the repository for the waste discharges of numerous industrial facilities and municipalities as well as urban and agricultural runoff. These surface supplies are also frequently sources of drinking water. Benzene and toluene for instance, is an organic compound which are found in drinking water from an eleven-city survey researches study and are considered carcinogens (Clark et al., 1989).

In a study, organic compounds such as benzene and toluene are often used to be removed by means of adsorption by the carbon process. These compounds were chosen

on a study of adsorption process using granular activated carbons because of the range of polarities these compounds shows, as well as their importance as environmental pollutants. These compounds are believed to be a good model for real world behaviors and application (Toles et al., 1997).

2.2 Adsorption

Processes of removing organic compounds such as the benzene and toluene from wastewater or organic solutions include the process of liquid phase adsorption. Adsorption is the process of accumulating substance that is in solution on a suitable interface. Adsorption is a mass transfer operation in that a constituent in the liquid phase is transferred to the solid phase. The adsorbate is the substance that is being removed from the liquid phase at the interface. In this case the adsorbate will be the toluene and benzene. The adsorbent is the solid, liquid, or gas phase onto which the adsorbate accumulates. Although adsorption is used at the air-liquid interface in the flotation process, only the case of adsorption at the liquid-solid interface will be consider.

The adsorption process has not been used extensively in wastewater treatment, but demands for a better quality of treated wastewater effluent, including toxicity reduction, have led to an intensive examination and use of the process of adsorption on activated carbon. Activated carbon treatment of wastewater is usually thought of as polishing process for water that has already received normal biological treatment. The carbon in this case is used to remove a portion of the remaining dissolved organic matter (Metcalf & Eddy, 2004).

Many adsorbent have been developed for a wide range of separations. Typically, the adsorbent are in the form of small pellets, beads, or granules ranging from about 0.1 mm to 12 mm in size with the larger particles being used in packed beds. A particle of adsorbent has a very porous structure with many fine pores and pore volumes up to 50% of total particle volume. The adsorption often occurs as a monolayer on the surface of the fine pores. However, several layers sometimes occur. Physical adsorption, or van der

Waals adsorption, usually occurs between the adsorbed molecules and the solid internal pore surface and is readily reversible.

The overall adsorption process consists of a series of steps in series. When the fluid is flowing past the particle in a fixed bed, the solute first diffuses from the bulk fluid to the gross exterior surface of the particle. Then the solute diffuse inside the pore to the surface of the pore. Finally, the solute is adsorbed on the surface. Hence, the overall adsorption is a series of steps (Geankoplis, 1993).

Theoretically, for *Pandanus amaryllifolius Roxb* leaves, due to its characteristics and the carbon network of the cell wall, the leaves are able to act as an adsorbent, thus adsorb the benzene and toluene.

Among the adsorbents, activated carbons are used more commonly in advanced wastewater treatment applications. Activated carbons are high porosity and high surface area materials. It can be produced from a number of precursor materials including coal, wood and agricultural wastes. These precursors are normally exposed to a number of different activation methods in an effort to achieve a carbon with the best qualities for a particular application (Toles et al., 1997).

Similarly, *Pandanus amaryllifolius Roxb* leaves which will act as an adsorbent to adsorb the organic compounds will undergoes a few pretreatment steps and drying techniques in achieving an adsorbent which could function expectantly for the purpose.

2.3 *Pandanus amaryllifolius Roxb* leaves.

Pandanus amaryllifolius Roxb leaves or better known as pandan leaves especially in Malaysia, are being used widely for several purposes. It is widely distributed in tropical and subtropical regions and many of it has been used for cooking or medicinal purposes. Some general information related to this plant is listed below.

Synonyms : Pandan wangi, *Pandanus odorus*, *P. Latifolius*, *Pandanus*, Umbrella tree, Screw pine, Screw tree, Dua thom, La dua.

Used plant part : Leaves, always used fresh (slightly withered). Even in their native area, pandanus leaves are often replaced by an extract that also contains green food colouring

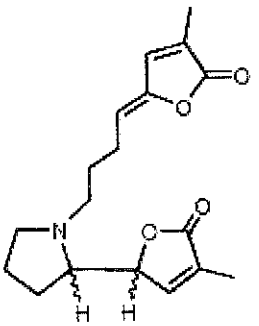
Plant family : *Pandanaceae* (screw pine family)

Main constituents : The flavour component of *pandanus* leaves is not well known. It is speculated that the flavour is due to a volatile product of oxidative degradation of a yellow carotenoid pigment that forms only when the plant whithers. In that respect, there are similarities to saffron and rose, which also contain caroteniod-derived aroma compounds.

Figure 2.1: *Pandanus amaryllifolius Roxb*

Besides these main constituents, another study found 3-methyl-2-(5H)-furanone as main volatile compound in pandanus leaves, besides 3-hexanol, 4-methylpentanol, 3-hexanone and 2-hexanone (Cancun, 1999).

The leaves also contain alkaloids, specifically pyrrolidine alkaloids. In a recent pharmacological survey, the hypoglycemic effect of the extract of *Pandanus odorus* was found. During a chemical study on the secondary metabolites in *Pandanus* plants, it is recently reported the isolation of new pyrrolidine alkaloids, pandamarilactonines-A and -B, from *Pandanus amaryllifolius Roxb* (Hiromitsu Takayama et al., 2001).



Pandamarilactonine-A, B (**1**, **2**)

Figure 2.2: Pandamarilactonines-A and –B structure of *Pandanus amaryllifolius Roxb*

Basically, an alkaloid is a plant-derived compound that is toxic or physiologically active, contains nitrogen in a heterocyclic ring, is basic, has a complex structure, and is of limited distribution in the plant kingdom. The nitrogen exist in the ring are usually derived from an amino acid. Alkaloids form water soluble salts. Most alkaloids are well-defined crystalline substances which unite with acids to form salts. In plants, they may exist in the free state, as salts or as N-oxides.

2.4 Effect of Pretreatment and Drying

A high porosity, high surface area materials are often used in industry for purification and chemical recovery operations as well as environmental remediation. These materials which often act as an adsorbent for an adsorption process can consist of many types of biomasses. For a process to achieve a desired rate of efficiency, these biomasses are preferably to be studied simultaneously treated. Physical pretreatment methods such as heating, autoclaving, freeze-drying and boiling, and chemical pretreatment had shown an enhancement or reduction in metal bioadsorption depending on the treatment and procedures used (Guangyu et al., 2000).

However, little was reported on the adsorption of organic compounds on plant based biomass, let alone the effect of pretreatment and drying on adsorption of benzene and toluene on Pandanus *amaryllifolius Roxb.* Previous studies have shown that chemical activation using acid at moderate temperature produces, in certain lignocellulosic material, a high surface area and a high degree of microporosity (Toles et al., 1997).

Other studies had shows that, in the case of alkali pretreatment, bioadsorption capacity was significantly enhanced due to the removal of surface impurities, rupture of cell membrane and exposure of available binding sites (Guangyu et al., 2000). However, there are also previous researches which show that these pretreatment methods may cause a reduction on the adsorption capacity. Pretreatments may destroy or change the structural characteristic of the biomass.

Drying method being applied is done for the purpose of increasing the adsorption capacity of the biomass. A high temperature condition would remove large amount of moisture content which accumulated in the adsorption site of the biomass. Removing these moisture content, produced a high porosity adsorbent with an increment of adsorption site will simultaneously enhance adsorption process.

In addition, there are also studies that are made which had a negative effect of drying towards biomass. It was reported that heat treatment could cause a loss of amino-functional groups on the fungal surface of a fungi based biomass through the non-enzymic Browning reaction (Whistler and Daniel, 1985). Here, it is studied that heat could also cause changes in biomass structure or loss of biomass reactive constituents.

2.5 Ultraviolet-Visible Spectrophotometer (UV-Vis)

Ultraviolet -Visible Spectrophotometer (UV-Vis) is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Its visible wavelength ranges of liquid are from 190nm to 900nm. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectrometer is usually applied to molecules or inorganic complexes in solution. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law. Since the UV-Vis range spans the range of human visual acuity, UV-Vis spectroscopy is useful to characterize the absorption, transmission, and reflectivity of a variety of technologically important materials, such as pigments, coatings, windows, and filters. This more qualitative application usually requires recording at least a portion of the UV-Vis spectrum for characterization of the optical or electronic properties of materials.

For analyzing process, data may be acquired in three basic modes: 1) wavelength scanning, 2) quantitative (single wavelength), and 3) time scanning. Post-analysis manipulation includes arithmetic manipulation, transformation of data and assignment to multiple file memory areas, and optimal data presentation on the screen. UV-Vis enables any combination of graphs, parameters, clipboards, and/or text on a single page which provides flexible output. (Foster et. al, 2003)

2.6 Gas Chromatography Mass Spectrometer (GCMS)

Gas chromatography is generally recognized as one of the most powerful separative methods available, and is widely employed in biomedical and environmental research. Although several selective detectors have been described, the identity of the separated components which elute must generally be inferred from their retention times relative to known standards. Mass spectrometry is a complementary technique in that it can provide a great deal of information about the identity of a compound provided that a pure sample is available, and may be sufficient to identify it rigorously. The combined system of GC and MS can utilize both instruments to maximum advantage and, under favorable conditions can identify every major component of a complex mixture.

The GC portion of this system provides high resolution separation of volatile organic solutes in a mixture in the gas phase. As each solute exits the GC column, it is diverted into a mass spectrometer which is capable of both monitoring the amount of and identifying the chemical nature of the solute. In this way, both quantitative and qualitative information about the mixture can be obtained.

The MS portion of the system takes each gaseous solute exiting the GC and ionizes it in an electron beam. The ions formed by a specific solute will depend on the nature of the bonds in the molecule, and both ionized molecules and ion fragments of the molecule are possible. The ions are then directed down a separator which isolates and counts the ions according to mass. The sequence and relative intensity of the mass peaks give information about the chemical identity of the solute. The absolute intensity of the peaks provides information about the amount of substance present (Tony, 2004).

2.7 Equation for the Uptake of the Organic Compounds and its Total Percentage Removal.

Analyzing equipment gives the result in terms of concentrations with units of parts per million (ppm). Thus, in studying the rate of adsorption, uptake of organic compounds from the initial solution similarly known as adsorbent phase concentrations need to be calculated using the equation as below.

$$Uptake, q(mg/g) = \frac{(C_i - C_o)}{m} V$$

Where,

C_i = Initial concentration of the solution (mg/L)

C_0 = Concentration of the solution at a specific interval of time (mg/L)

m = Mass of adsorbent (g)

V = Volume of solution (L)

The adsorbent phase concentration data computed are then used for analyzing and comparison (Metcalf & Eddy, 2004).

At the end of the test period of the adsorption process, the amount of adsorbate remaining in solution is measured. Total percentage removal of the organic compounds are computed using,

$$Total\%removal = \frac{(C_i - C_f)}{C_i} \times 100$$

Where,

C_i = Initial concentration of the solution (mg/L)

C_f = Final concentration of the solution (mg/L)

CHAPTER 3
METHODOLOGY / PROJECT WORK

3.1 Procedure Identification

3.1.1 Preparation of *Pandanus amaryllifolius Roxb* Leaves

Pandanus amaryllifolius Roxb leaves were collected from the area of Gunung Rapat, Ipoh, Perak. The sample was thoroughly rinsed with distilled water. The leaves were ground in a laboratory grinder and sieved to a 600 μm-1.18 mm range particle sizes using the sieve shaker. The sample was then kept in airtight bottles. These preparations are used for the purpose of preparing the untreated and pretreated biomass. Method used had been extracted from the studies done by Toles et al. (1997).

3.1.2 Preparation of Wastewater and Pretreatment Solution

Benzene and Toluene solution were prepared at concentrations above the maximum contamination limit *(refer **Appendix A**)* of both compounds which is 5 ppm. Pure solutions of both compounds were diluted and a solution of 1000 mL each was prepared initially. (Amount of each solution used was more than 1000 mL)

Hydrochloric acid (HCl) and sodium hydroxide (NaOH) used for the pretreatment purposes were prepared at a minimum concentration of 0.1 M by diluting its pure solutions. *(Refer **Appendix A** for the sample calculation of the solutions).*

3.1.3 Effect of Pretreatment

The biomass is mixed in acid/base solutions and allowed to soak for ½ hours at room temperature. Approximately, the samples were placed in an oven at an ambient temperature of 30°C for 48 hours. After being dried, the samples were then kept in airtight bottles ready to use as an adsorbent for the adsorption process.

3.1.4 Effect of Drying

Pandanus amaryllifolius Roxb leaves which were collected were rinsed with distilled water and dried in the oven at a temperature and time which varies accordingly to sample being set.

Table 3.1: Effect of Drying at Constant Drying Time (24 hours)

Sample	Temperature (°C)
1	50
2	80
3	120

The leaves were ground in a laboratory grinder and sieved to a 600 μm-1.18 mm range particle size using the sieve shaker. The sample was then kept in airtight bottles. Moisture contents in each of the biomasses at respective dried temperature are being analyzed manually by measuring the weight of biomass before and after drying.

3.1.5 Biomass Analysis

Before the adsorption process proceeds, the biomass was initially analyzed to determine its respective porosity and the moisture content. The porosity was determined manually. As the first step, the total volume of the fixed bed is being determined. The biomass is placed in the fixed bed at a specified biomass weight and column height. Water is then being introduced inside the bed to the same column height as the biomass. For this step, the discharge outlet of the bed is being closed. As the water is at the same height as the

biomass, the water is then being discharge out of the bed and its volume being measured. Porosity of the biomass was calculated using the equation below.

$$Porosity, \varepsilon = \frac{(V_o - V_w)}{V_o}$$

Where,

V_o = Total volume of the fixed bed (m^3)

V_w = Volume of water being discharged out of the bed (m^3)

3.1.6 Adsorption Process

2g of biomass (untreated, pretreated and dried) is placed in the chromatography column at a specific height (6 cm). The column was held by a retort stand. The simulated wastewater solution was pumped at 40 ml/min using a peristaltic pump for four hours duration. The filtered solution is collected at the bottom of the bed at specific time intervals and stored in the refrigerator at 2°C. The solution is analyzed using the Ultraviolet-Visible Spectrometer (UV-Vis) and Gas Chromatography Mass Spectrometer (GCMS) to check for the remaining adsorbate (organic compounds). The intervals of time used to take the samples are tabulated in the tables below.

Table 3.2: Intervals of Samples Time

Sample No.	1	2	3	4	5	6	7	8	9
Time (min)	5	10	15	20	25	30	45	60	75

Sample No.	10	11	12	13	14	15	16	17	18
Time (min)	90	105	120	135	150	165	180	210	240

3.1.7 Analyzing

The concentration of benzene was analyzed by using the Ultraviolet-Visible Spectrophotometer (UV-Vis) equipment.

Toluene on the other hand is analyzed using UV-Vis and GCMS. For both equipments, standards were prepared at 1ppm, 3ppm and 5ppm. Wavelengths for both solutions are being determined for the used of detecting concentration by UV-Vis.

CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 Results

4.1.1 Biomass

4.1.1.1 Moisture Content

The biomass moisture content is analyzed manually by measuring the weight of biomass before and after drying. The results are as tabulated below.

Table 4.1: Percentage Removal of Moisture Content for Biomass with Drying Effect

% of Moisture Removed in the Biomass			
50 °C	80 °C	120 °C	Untreated
94.4%	96.4%	99.6%	46.5%

4.1.1.2 Porosity

The porosity of the biomass (untreated, pretreated and dried) is analyzed and the result is as shown below.

Table 4.2: Porosity of Biomass with Different Effects

Porosity, ε					
Untreated	HCl	NaOH	50 °C	80 °C	120 °C
0.48	0.57	0.52	0.56	0.62	0.64

4.1.2 Observations

The treated solution was observed to be dark brown/yellow in color at an interval time of 5 minutes to 20 minutes. After this duration of time, the treated solution is colorless.

4.1.3 Benzene Analysis

Benzene concentration in the solution was determined using the UV-Vis. The data obtained was analyzed and trend of adsorption was obtained. (*Refer **Appendix B** for the raw data of benzene obtained from UV-Vis analysis).*

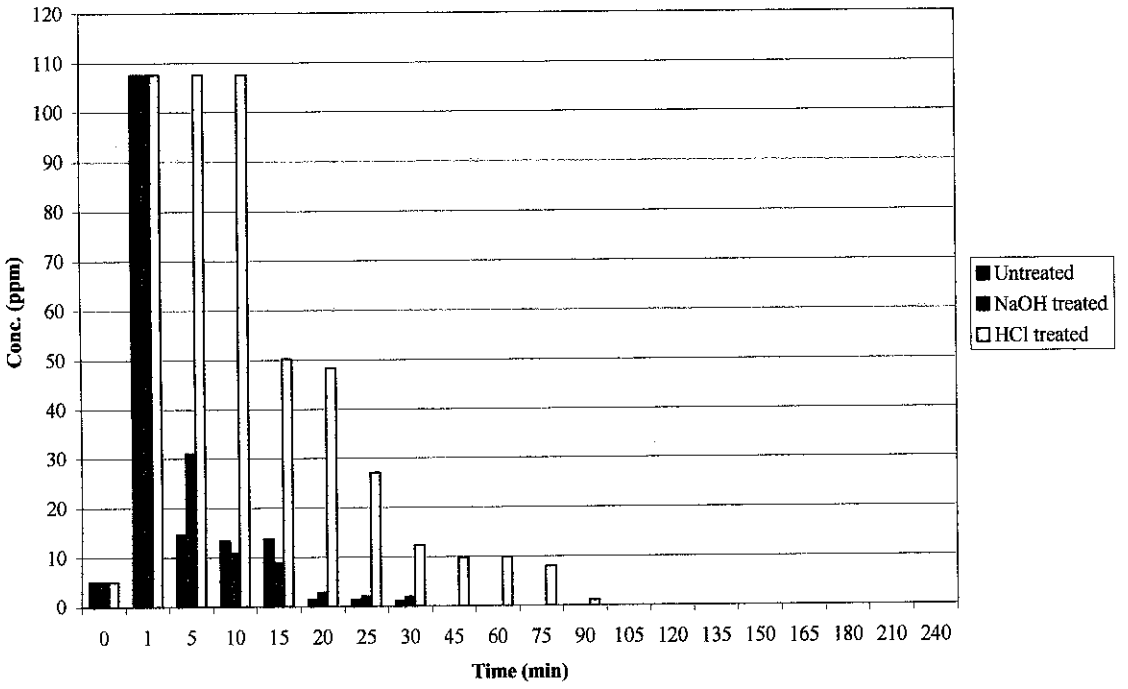


Figure 4.1: Benzene Concentration in the Solution after Adsorption for the Untreated and Treated Biomass

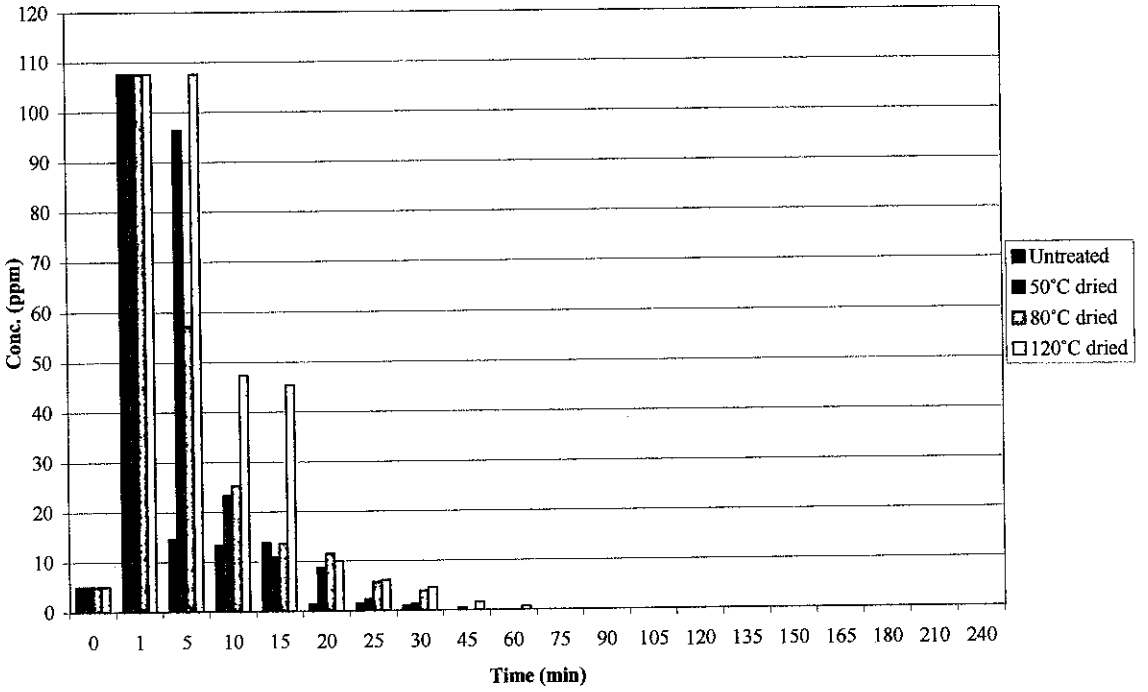


Figure 4.2: Benzene Concentration in the Solution after Adsorption for the Untreated and Dried Biomass

4.1.4 Toluene Analysis

Toluene concentration was determined using both the UV-Vis and GCMS. The data obtained was analyzed and trend of adsorption was obtained. (*Refer **Appendix C** for the raw data of toluene obtained from UV-Vis analysis).*

4.1.4.1 UV-Vis Analysis

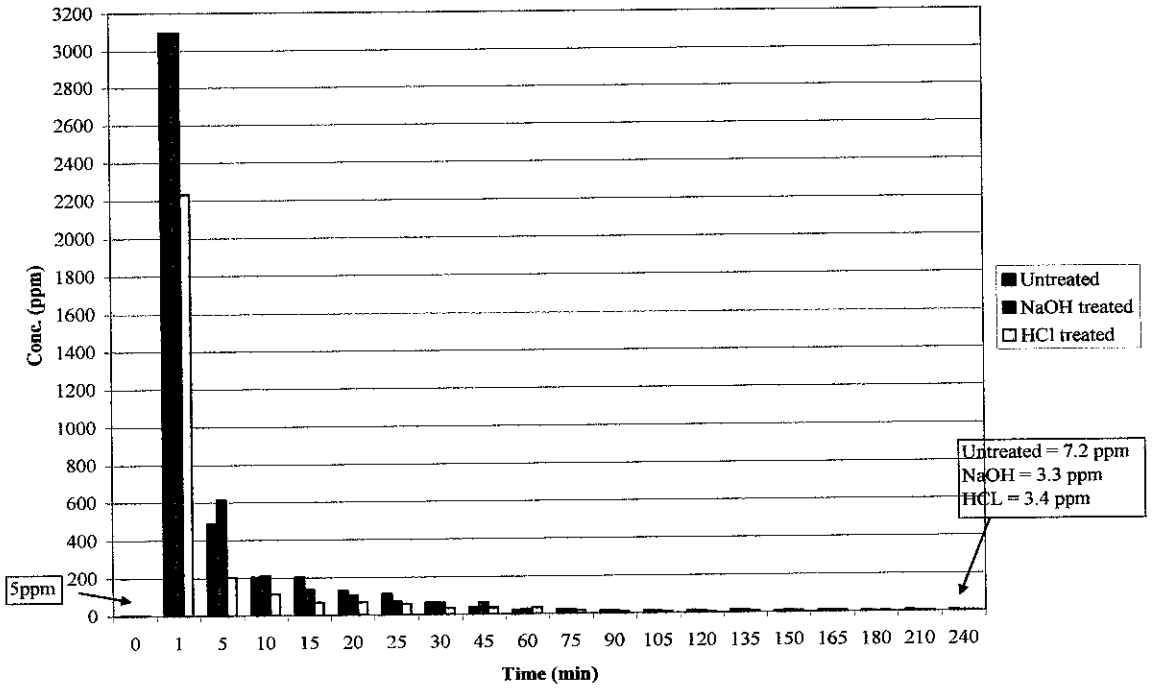


Figure 4.3: Toluene Concentration in the Solution after Adsorption for the Untreated and Treated Biomass

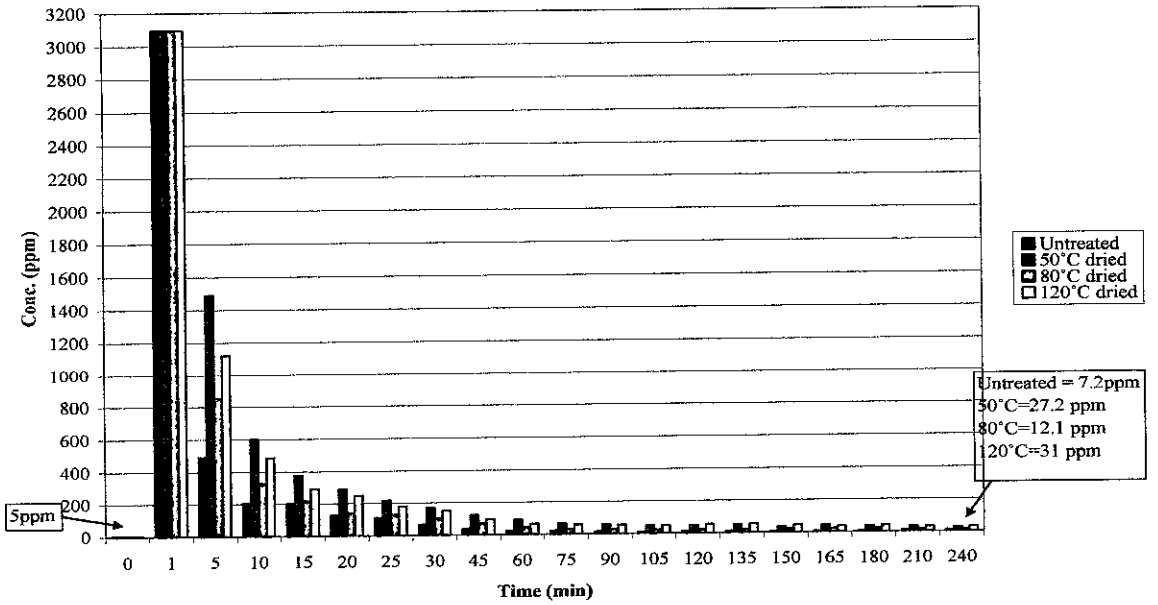


Figure 4.4: Toluene Concentration in the Solution after Adsorption for the Untreated and Dried Biomass

4.1.4.2 GCMS Analysis

For the GCMS Analysis, the data was analyzed in terms of concentration of toluene in solution and the uptake of the compound by the biomass. (***Refer Appendix D*** *for standard calibration curves of toluene).* Comparison between untreated and treated biomass for the uptake of toluene are analyzed from graphs below.

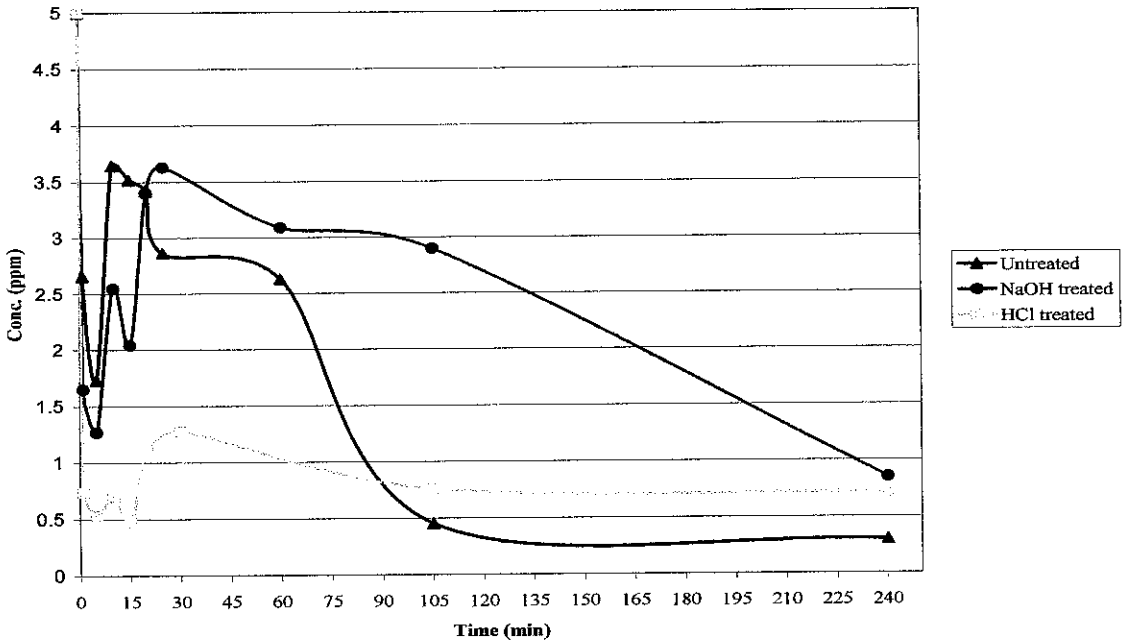


Figure 4.5: Toluene Concentration in the Solution after Adsorption for the Untreated and Treated Biomass

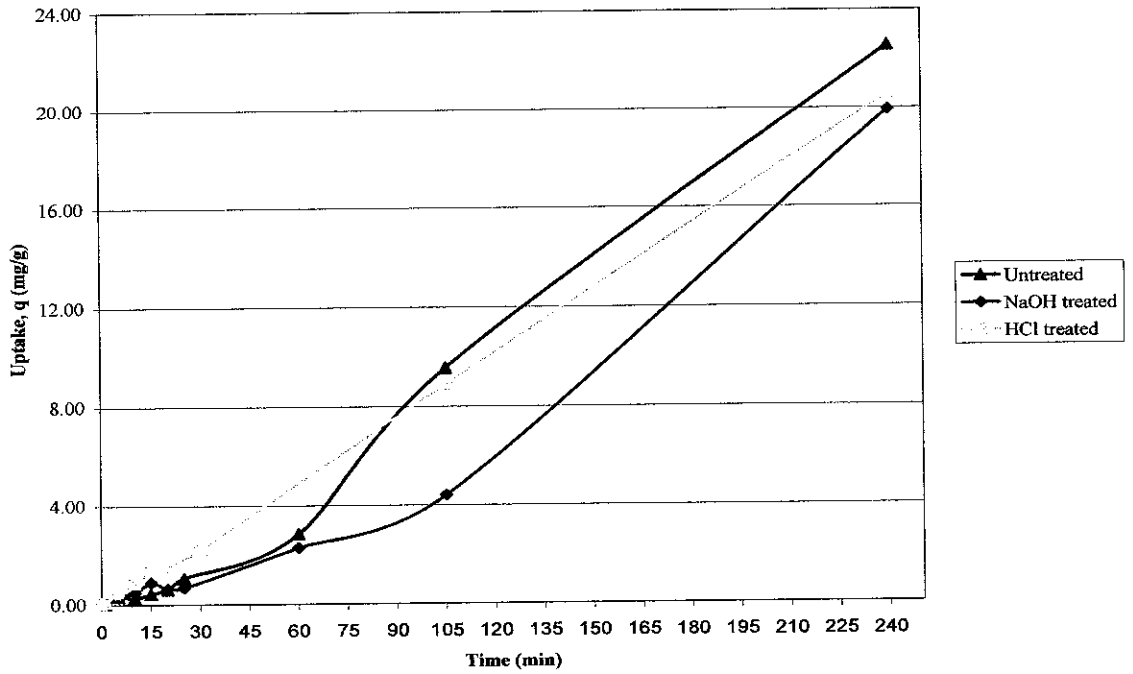


Figure 4.6: Toluene Uptake for Untreated and Treated Biomass

The concentration and uptake of toluene for the biomass with drying effects are being summarizes in graphs below.

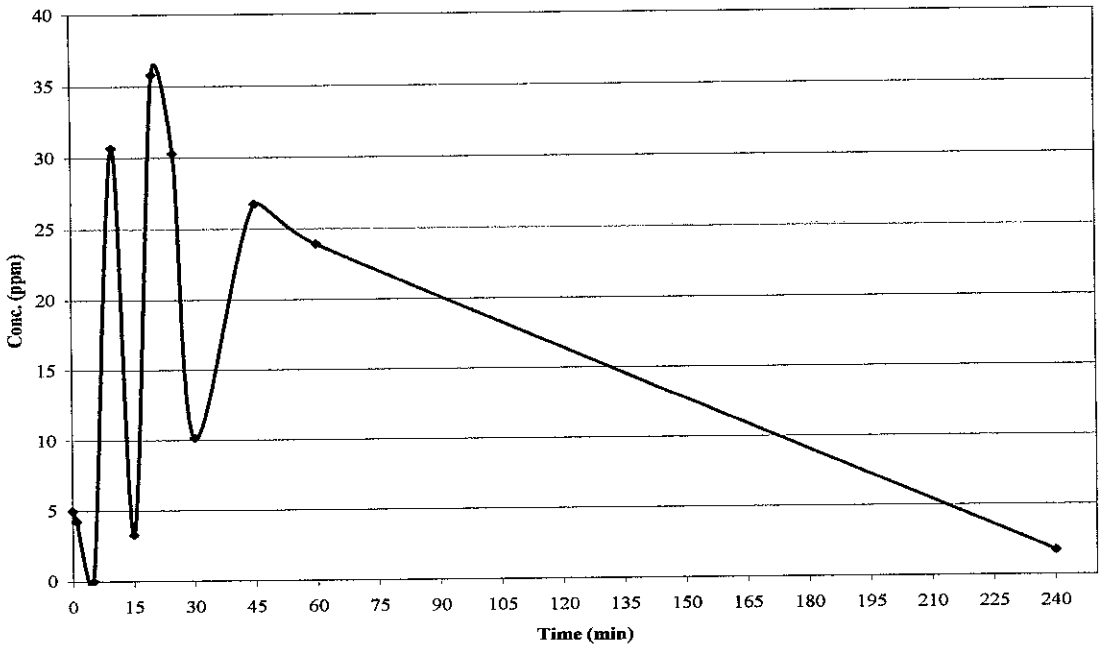


Figure 4.7: Toluene Concentration in the Solution after Adsorption for Biomass Dried at 50°C

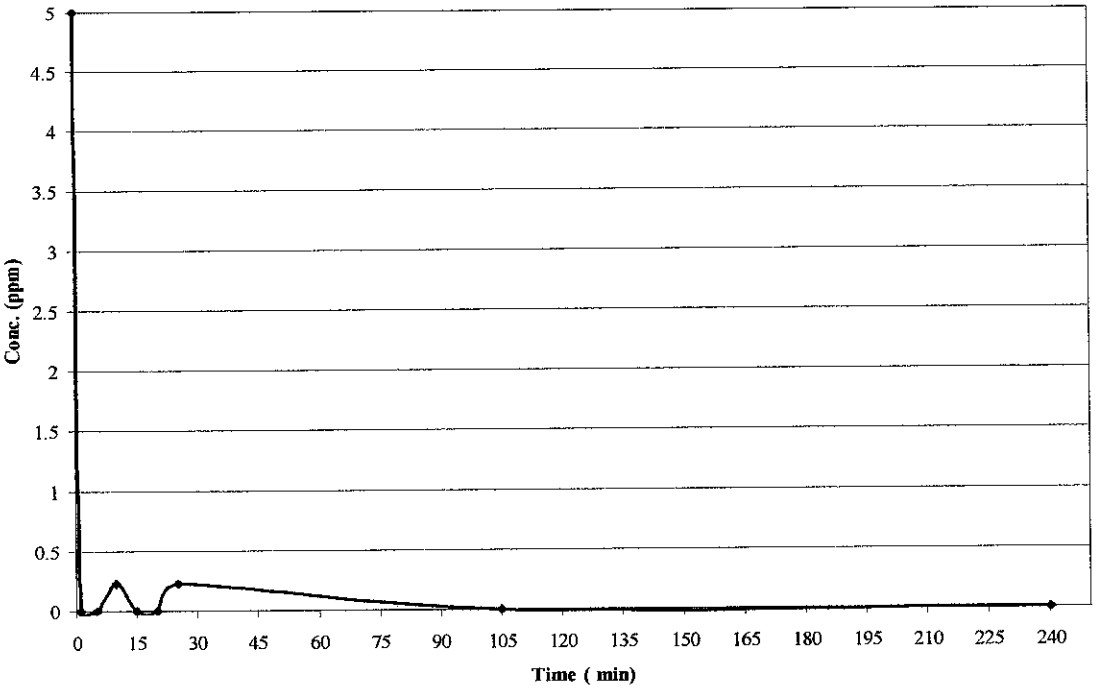


Figure 4.8: Toluene Concentration in the Solution after Adsorption for Biomass Dried at 80°C

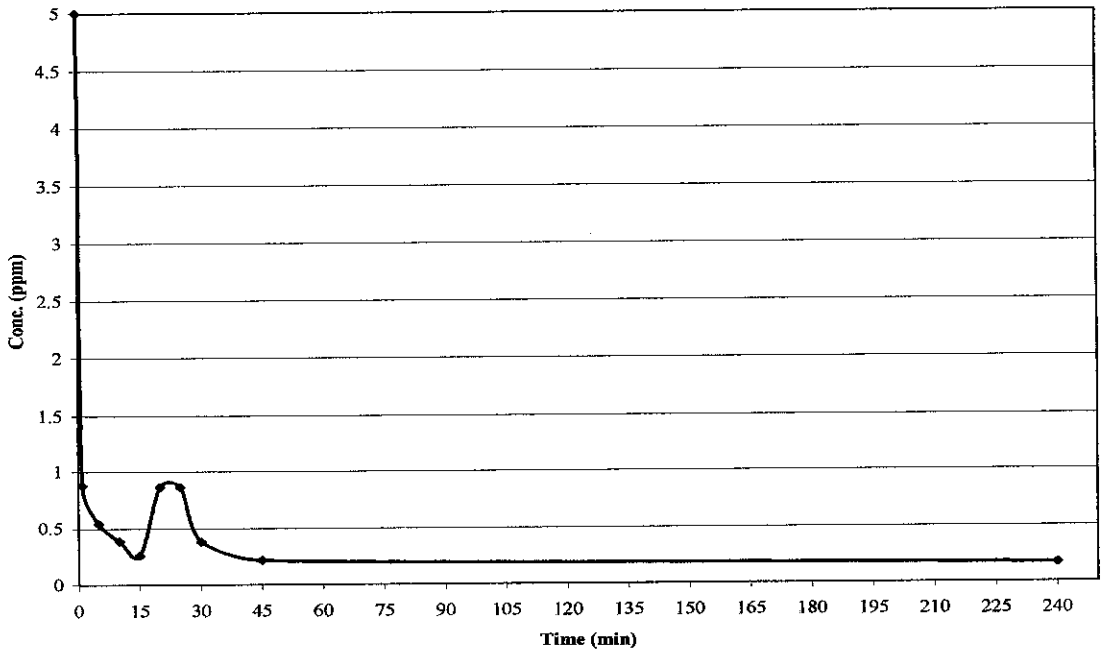


Figure 4.9: Toluene Concentration in the Solution after Adsorption for Biomass Dried at 120°C

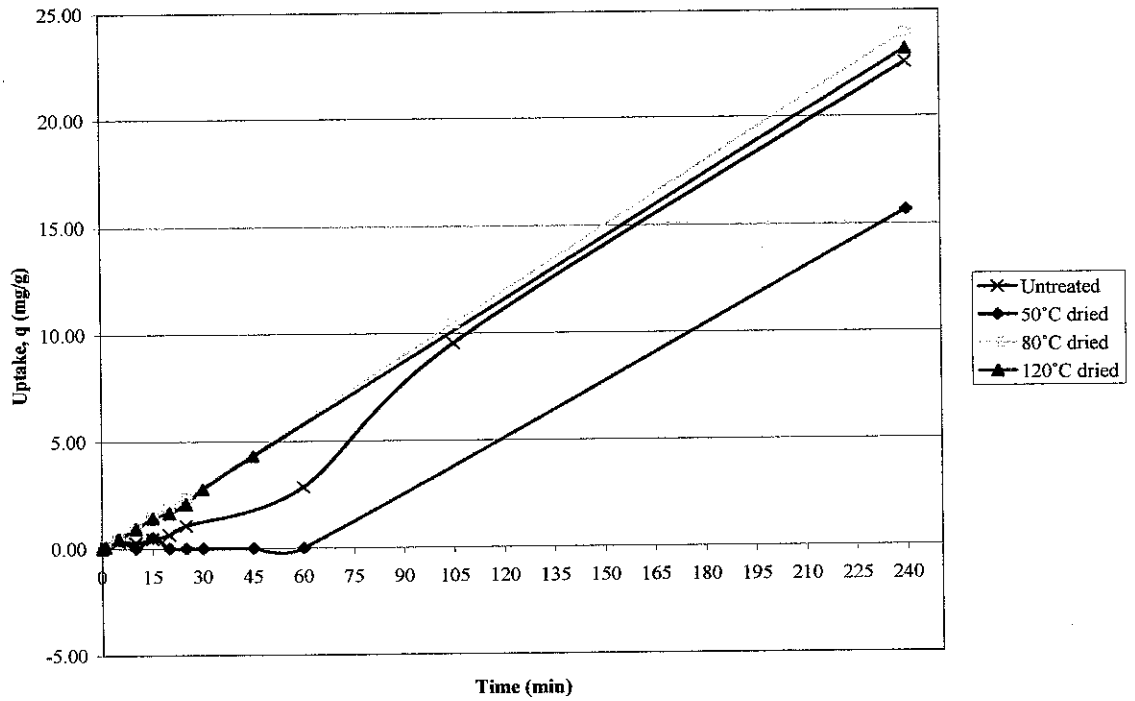


Figure 4.10: Toluene Uptake for Untreated and Dried Biomass

4.1.5 Total Percentage Removal

After each of the experiment been completed and analyzed, the total percentage removal of the organic compound are being determined.

Table 4.3: Total Percentage Removal of Benzene and Toluene

	Total % Removal					
	Untreated	Treated with HCl	Treated with NaOH	Dried at 50°C	Dried at 80°C	Dried at 120°C
Benzene	100% (45 min)	100% (105 min)	100% (45 min)	100% (60 min)	100% (45 min)	100% (75 min)
Toluene	94%	85.70%	83%	65.20%	100%	96.60%

Total percentage removals of benzene for biomasses with both effects, are being analyzed and compared as per below.

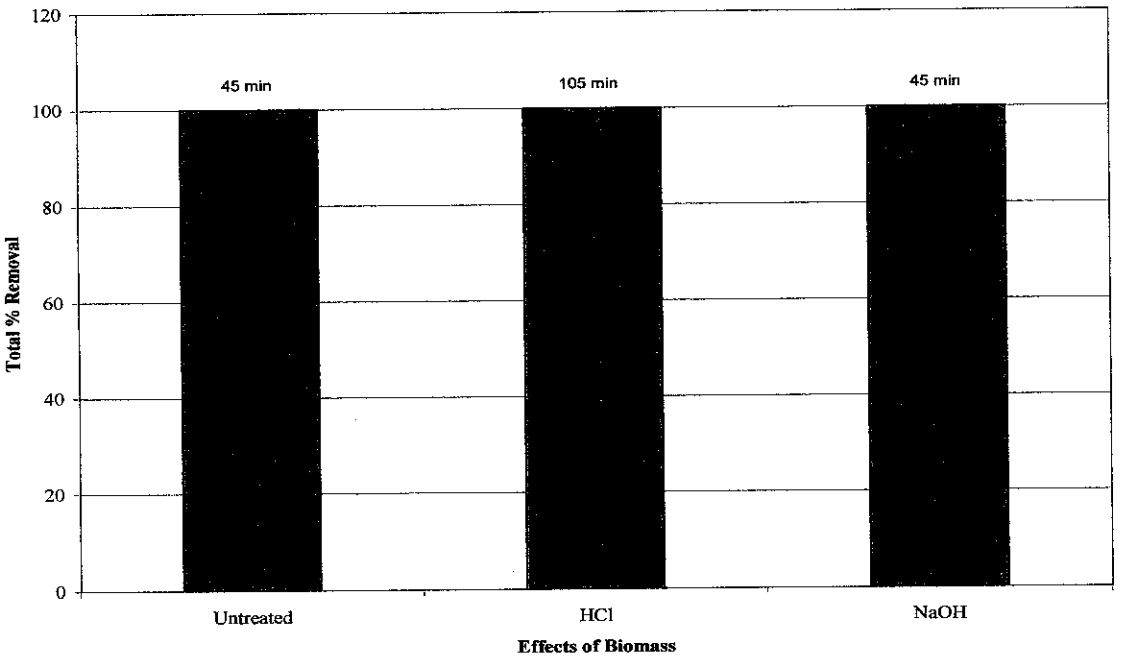


Figure 4.11: Total % Removal of Benzene for Biomass with Pretreatment Effect

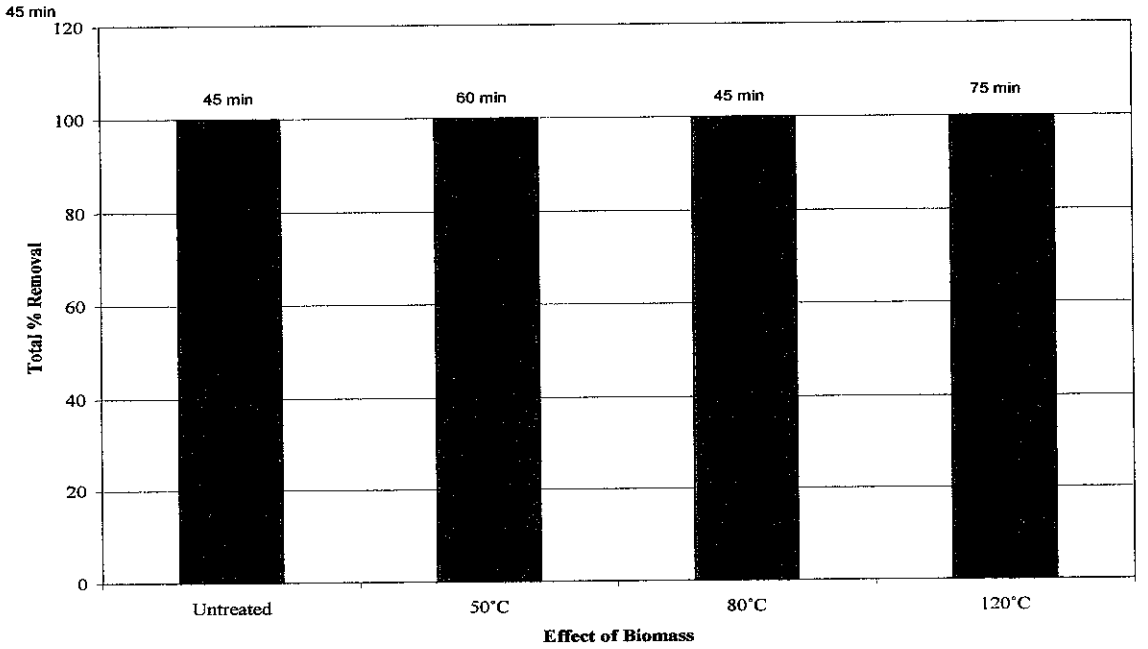


Figure 4.12: Total % Removal of Benzene for Biomass with Drying Effect

Total percentage removals of toluene for biomasses with both effects, are being analyzed and compared as per below.

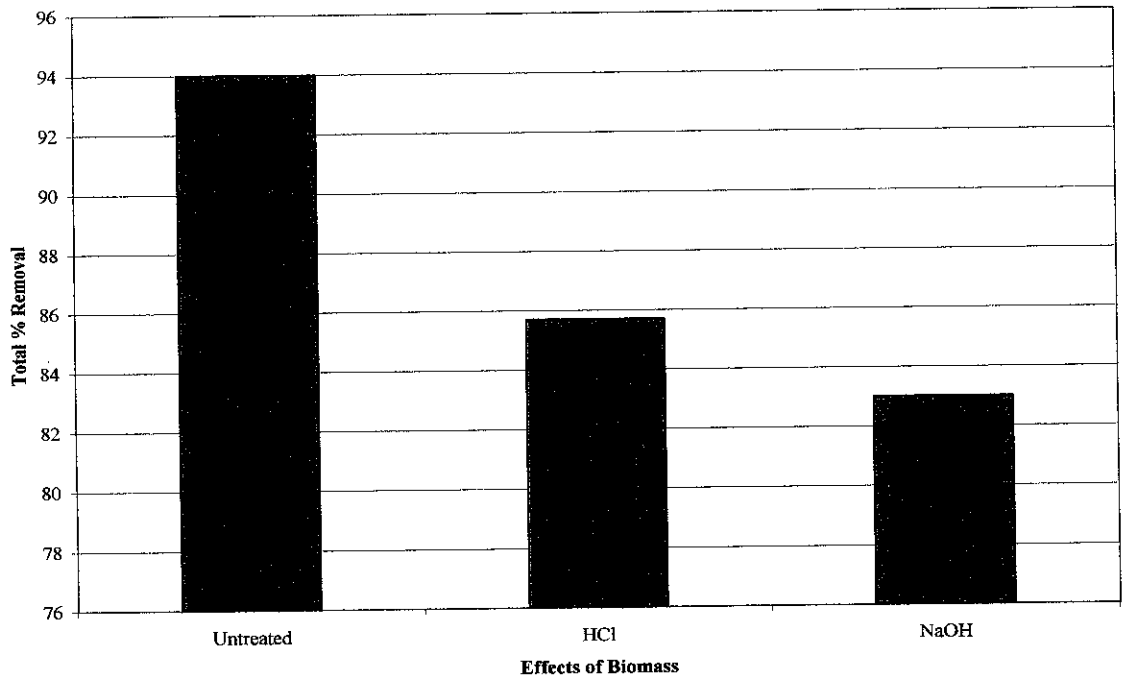


Figure 4.13: Total % Removal of Toluene for Biomass with Pretreatment Effect

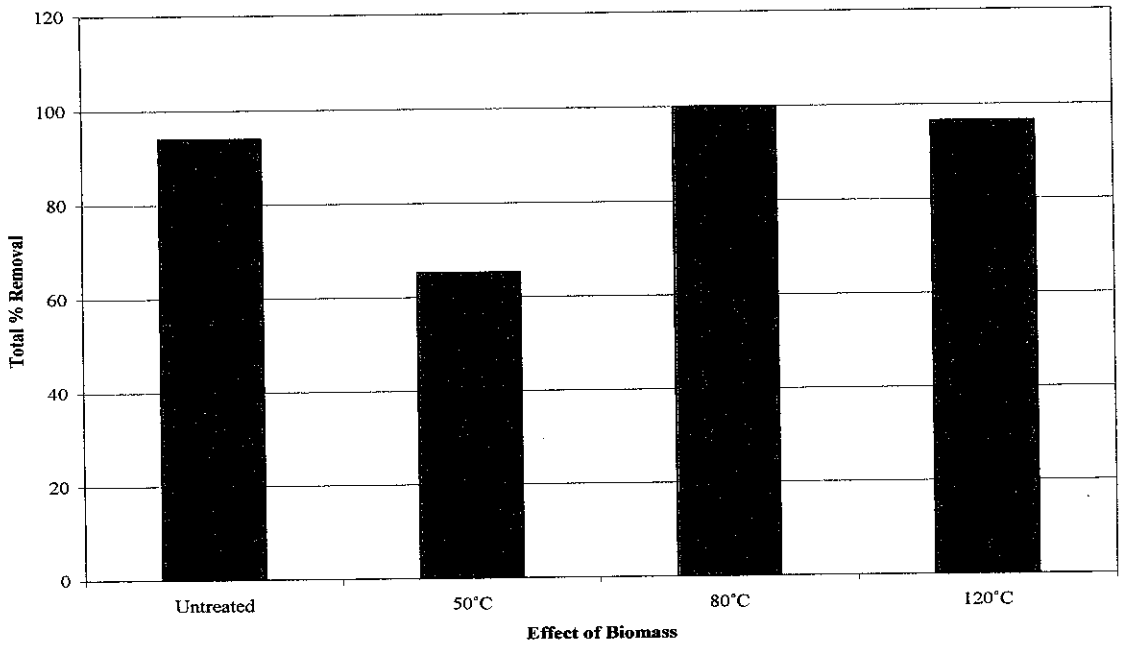


Figure 4.14: Total % Removal of Toluene for Biomass with Drying Effect

4.2 Discussions

4.2.1 Benzene Analysis

The results show that through fixed bed adsorption process, the removals of benzene can be done. Concentration of benzene decreases as time increases (**Figure 4.1** and **4.2**). Each effect being applied to the biomass had resulted in a different trend of adsorption. Similarly, all effects shows that the benzene had been removed 100% from the wastewater solution. The difference is in term of adsorption time. It is analyzed here that the fastest rate of adsorption occurs for the untreated, treated with NaOH and dried at 80°C biomass. At an interval time of 45 minutes, the benzene had been completely removed.

4.2.1.1 Effect of Pretreatment

Comparing in terms of pretreatment effects, it is observed that by treating the untreated biomass with NaOH, the adsorption rate almost maintained or reduced to a small extent of the adsorption of benzene in comparison with untreated biomass. In terms of porosity, treatment with NaOH had increased the porosity to 0.570 (**Table 4.2**). Although it is a 100% removal after 45 minutes of adsorption, it is seen that untreated biomass shows a larger decrement than NaOH treated biomass at intervals of time before the 45 minutes. At 30 minutes, for example, the concentration of benzene for untreated biomass is at 1.0ppm where as for NaOH treated biomass is at 1.9ppm. Studies show that in the case of alkali pretreatment, bioadsorption capacity was significantly enhanced. In a study by Galun et al. (1987), NaOH treated *Penicillium digatatum* showed enhancement in bioadsorption of heavy metals. It shows that pretreatment done with NaOH or other alkali, will removed the surface impurities, rupture of cell membrane and increases the exposure of available adsorption site (Guangyu et al.,2000). The researches are significant for heavy metals adsorption which involves ions for the adsorption process. For this study, the trend shows that untreated biomass had a significantly higher rate of adsorption in comparison with NaOH treated biomass. Although adsorption site are

theoretically to be expand, in the case of organic compound, NaOH may change the structure of the biomass to an extent that doesn't allow organic compounds to be adsorb efficiently. However both are efficient enough in removing benzene from a solution.

Acid pretreated biomass significantly decreased the adsorption of benzene compared to untreated biomass and NaOH treated biomass. Unlike untreated and NaOH treated biomass which shows 100% removals at 45 minutes, HCl treated biomass takes a longer period of 105 minutes to removed the benzene by a total of 100%. Its biomass porosity is 0.52 which is slightly larger than raw biomass's porosity. A researches shows that the H^+ ions (from acid pretreatment) binding to the biomass after acid treatment may be responsible for the reduction in adsorption rate. The polymeric structure of biomass surface exhibits a negative charge due to the ionization of organic groups and inorganic groups (Hughes and Poole, 1989). The H^+ ions on the acidic pretreated biomass may change the structure and the surface area of the biomass.

4.2.1.2 Effect of Drying

For the time based the temperature which are varies consists of 50°C, 80°C and 120°C. 80°C are chosen as it is a moderate temperature for the biomass to be activated without damaging the plant structure. It is studied that if the biomasses are exposed to a high heat, some part of the carbon mass may be loss and efficiency of the biomass to adsorb organic compound may be reduced. 50°C are chosen as to see whether it is enough to remove sufficient moisture for the adsorption process to happen more accurately. 120°C of heating is to observe would the biomass still can actively act as an adsorbent at a high temperature or does it changes all the plant structure that it can no longer adsorb the organic compound. It is observed here that by heating the biomass at 80°C gives the highest rate of benzene adsorption by the biomass. Similar to both untreated and NaOH treated biomasses, the total percentage removal of this organic compound is 100% at 45 minutes compared to 50°C at 60min and 120°C at 75 minutes.

Content of moisture exist in the biomass may cause in the reduction of adsorption site. Thus, theoretically, by removing the moisture content, adsorption efficiency should be higher due to larger area of adsorption site. Porosity measurements show that an increment of temperature will result in an increment of porosity (Table 4.2). Biomass dried at 120°C had increases the porosity up to 0.64 compared to biomasses being dried at 50°C and 80°C which are 0.56 and 0.62. With references to the commercializes activated carbon which are often used in removing organics compounds, its high efficiency of adsorbing materials is due to its high porosity characteristics (Geankoplis, 1993). Hence, a large porosity is desirable to result in a higher rate of adsorption. However, results show that biomass dried at 120°C which moisture content had been removed by 99.55% had the least adsorption efficiency in comparison with the other two temperatures. It was studied that the high heat being exposed to the biomass may result in a total burned off and loss of some part of carbon mass. At 80°C would be the best temperature for heat supplied as it gives the highest rate of adsorption. However, in comparison with untreated biomass, the rate of reduction is much lower at intervals of time before it reaches 100% removals.

4.2.1.3 UV-Vis Analysis

Graphs of concentration of benzene in solutions versus time obtained from data's analyzed by UV-Vis, shows errors in readings. It is observe that for the first 20 minutes, the concentration increases above the initial concentration which is 5ppm. After this duration of time, the concentration decreases in a trend below the initial concentration.

Ultraviolet - Visible Spectrophotometer (UV-Vis) is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. It measures the degree to which light is adsorbed, or the intensity of the light that is emitted and it is related to the amount of an analyte present in the sample tested. When there is a large number of contaminant existed in the sample tested, errors in readings will happen. These contaminants will cause interferences that give an absorbance signal at the same wavelength or wavelength range selected for analyte. As

UV-Vis measurement is related to color, changes of color in the sample test will effects its measurement of the attenuation of a beam of light. Thus, for an accurate measurement, the sample must be of clear and contaminant-free.

The sample of the purified solution initially, as mentioned, is of dark brown in color. It is studied that these changes in color may be an attribute from the contaminant and other unknown particles that might be carried over by the solution from the biomass. Benzene is a highly concentrated solvent. Solvent acted as to extract a portion of solution or particles from other solutions. Introduction of this solvent, to the biomass, may cause a separation of many contaminants or constituents that may exist in the biomass itself. Among the constituents that may exist in the biomass that may be extract by the solvent are the yellow carotenoid pigment, the alkaloids which might be in a soluble salt forms, chlorophyll and other particles (Cancun, 1999).

4.2.2 Toluene Analysis

4.2.2.1 UV-Vis Analysis

Toluene existence in solution was initially analyzed using the UV-Vis. Result obtained from this equipment shows a larger error compared to when it analyzed the concentration of benzene. The result shows an increment up to 3000ppm at the first minutes but decreases as time increased (**Figure 4.3** and **4.4**). However, each reading with exception of readings for the biomass with the effect of pretreatment does not decrease below than the initial value which is 5ppm. Beside contaminant and color changes sees on the sample being tested as explained earlier, one of the major contributions comes when running the standard solution of toluene using the UV-Vis. The standard solution was prepared at 1ppm, 3ppm and 5ppm. These solution, as being tested by UV-Vis, does not shows any peak of toluene and no calibration curve could be calibrated from it. Thus, the concentration of standard solution was increased up to more than 5ppm. Here, it shows the equipment presents the toluene peak and analyzing were conducted for all sample

using the calibration curve being calibrated from the standards. Somehow, these standards affect the readings of the solutions.

However, despites the errors it gives for the readings, it is observe that the concentration decreases over time for all adsorption process with different effects. Thus, in obtaining more accurate readings for analyzing each effect, Gas Chromatography Mass Spectrometer are used to analyzed the toluene existence and concentration.

4.2.2.2 GCMS Analysis

Using a standard of 1ppm, 3ppm and 5ppm, GCMS gives the relative intensity of the mass peaks identified to be toluene at respective concentration. Using these peaks, calibration curve are made in order to analyzed and detect the exact amount of toluene which would exist in the sample test. Results are being presented in a graph of concentration of toluene versus time and its uptake over time.

Similar to UV-Vis analysis, each adsorption process with different effect of biomass shows a decrement of toluene in the solutions. GCMS gives a decrement of below the initial concentration and resulted in a more accurate value.

Observing the graphs of the uptake of toluene versus time (**Figure 4.6** and **4.10**), the uptake of toluene for each effect is almost proportional to time. As time increases, the uptake increases. By calculation each effect had removed the toluene to more than 50% the initial concentration and effect of drying at 80°C had shown a 100% removal of toluene.

Comparison in terms of rate of adsorption for different effects of biomass shows that biomass being dried at 80°C has the highest rate of adsorption simultaneously means the adsorption site here is the largest. It is discussed that by removing the moisture content to 96.4% would provide a large porosity and high capacity of adsorption in the biomass. At 50°C, the rate of adsorption is the lowest with total percentage of toluene

removals of 65.2%. Although the moisture content being removed which is at 94.4 % is not much difference from heating at 80°C, the adsorption capacity shows large differences. This may be explained by the series of steps of adsorption inside the adsorbent. It is studied that when the fluid is past through the fixed bed, the solute first diffuses from the bulk fluid to the gross exterior of the particle. Then the solute diffuses inside the pore to the surface of the pore. Finally, the solute would be adsorbed on the surface (Geankoplis, 1993). It is assume that the moisture that may have remained inside the biomass may have accumulated the inside surface of the pore which would prevents toluene to be adsorb efficiently inside the surface of the pore.

Similar to benzene analysis, for drying effect at 120°C, even with a high porosity, the rate of adsorption is lower than 80°C with a total percentage of toluene removal at 96.6% **(Table 4.3** and **Figure 4.14)**. Whistler and Daniel (1985) reported that heat treatment could cause a loss of amino functional groups on the fungal surface through the non- enzymic Browning reaction. It shows here that heating of biomass could change its structure and resulted in loss of some active constituents. It applies to the heating of *Pandanus amaryllifolius Roxb* at a high temperature which could cause a reduction of cell reactivity towards adsorption.

Effect of pretreatment, had resulted in a much lower rate of adsorption being compared to untreated biomass. The uptake of toluene for the effect of pretreatment reaches 20 mg/g compared to uptake of toluene using untreated biomass which reaches 23 mg/g. As mentioned earlier, pretreatment could remove the surface impurities, rupture of cell membrane and a larger exposure site for adsorption which would enhance adsorption capacity. This may be the reactions happens in the biomass as it is being pretreated but along with it, the structure of the carbon network for the binding of toluene inside the biomass may be removed or changed resulting in a less efficient adsorption.

Observing the graphs of concentration of toluene in solution versus time (**Figure 4.5, 4.7, 4.8** and **4.9**), each shows a decrement of concentration in the final solution. The trend of the graphs although decreases over time, does not shows a constant decrement.

Graphs for all effects had shown that during the first 5 to 10 minutes toluene concentration had drop drastically but increase simultaneously at duration of 15 to 25 minutes. After these intervals, the concentration decreases constantly over time. Hypothesis and assumptions were made on the initial trends shows on each graph.

The trends shows as above are assumed to be related to the dryness of the biomass bed. As the toluene being first introduced, the biomass is in a dry state. Thus, adsorption capacity is high. Toluenes are adsorbed in a large amount of concentration at a duration time of the first 10 minutes. After this duration of time, as the contact time between toluene and the biomass increases until certain minutes, the initially adsorbed toluene in the biomass are assumed to be carried down as a purified solution to be tested. This may happen during the first 15 to 25 minutes where the graph shows a sudden increment, as initial stage of fixed bed adsorption process is where the process is most unstabilized. Duration of 30 minutes and above had shows a constant decrement of toluene concentration which tells that the process is more stable where the biomass now used to adsorb is in the same state of condition throughout the process unlike the initial state of condition where it changes from dry to moist.

Another possible cause that may contribute to this result is the constituents that may exist in the biomass itself. As mentioned in the literature reviews, in *Pandanus amaryllifolius Roxb* biomass, there are numbers of constituents, both known and unknown. Toluene as solvent on the other hands has many functions. From the molecular-microscopic point of view, solvents break the crystal lattice of solid reactants, dissolve gaseous or liquid reactants, and they may exert a considerable influence over reaction rates and the positions of chemical equilibria (George Wypych, 2000). Initially, the dry state of biomass may contain constituent which are already exist as a part of *Pandanus amaryllifolius Roxb* leaves and contaminants that may come from the surrounding of the biomass origin. This unknown particles, either chemically or physically may have reacts with the toluene as it is first introduced inside the bed. Reactions that may occur may change the characteristics or structure of this solvent resulting in varies of undetectable constituent peaks shows in GCMS analysis. Instead of

toluene being adsorb in the initial state, the solvent might be restructured to another form of substances. As duration of time lengthens most of the constituent and contaminants have been carried over, leaving the biomass to have a larger exposure of adsorption sites for adsorption to happens.

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The project main objective is to study the removal of benzene and toluene by using *Pandanus amaryllifolius Roxb* leaves which is believed to be feasible for organic compound removal due to its carbon network of the cell wall. It is to see the capability of the *Pandanus amaryllifolius Roxb* leaves as an adsorbent to remove the organic compounds in a fixed bed adsorption process. Also, the research was done to see the effect of pretreatment and drying towards the uptake of benzene and toluene from the wastewater. Through these studies it shows that using *Pandanus amaryllifolius Roxb* leaves as adsorbent, removals of benzene and toluene could be accomplished. Optimum conditions for adsorption to happen were obtained. Over time, it is observed that both organic compounds decreases as it came in contact with the biomass. Rate of adsorption for different effect of biomass were identified. *Pandanus amaryllifolius Roxb* leaves are found to remove benzene much better than removing toluene. For benzene, although effect of pretreatment and removals of moisture content are being applied to the biomasses, the result shows that the optimum condition for adsorption to occur is by using the untreated biomass as the adsorbent. In the case of toluene, removals reach an optimum level as biomass was dried at 80°C. In conclusion, through fixed bed adsorption process using *Pandanus amaryllifolius Roxb* leaves as an adsorbent, benzene and toluene were removed and both pretreatments and drying effect had resulted in a different rate of removals.

5.2 Recommendations

Pandanus amaryllifolius Roxb leaves being used in the project are not free from contaminants. These unknown contaminants brought along from the origin of the leaves cause several errors throughout the project. Although pretreatments which have the purpose of removing these contaminants are being undergoes in the project, results does not shows a significant improvement towards the uptakes. One of the reasons is that the leaves are being pretreated without knowing the type of contaminant that may exist in the leaves. It is suggested, that a study on the leaves itself was to be done. The types of unknown particles and contaminants inside it have to be identified so that pretreatment could be done using a much more suitable chemical.

UV-Vis is highly recommended equipment in analyzing volatile organic compound quantitatively. Measured in an error-free conditions could give an accurate amount of respective compounds. Any interference such as contaminations of samples, may divert the effect and gives inconsistent readings. One of the major contaminants in the project comes from the color of the samples. It is recommended that a method of decolorization is applied to the colored solutions. A clear, color-free solution would result in accurate readings. However, decolorization may affect the compound to be measured which exists in the solutions. Thus, a method needs to be carefully analyzed as to be used without having interferences towards the compounds to be measured.

Measuring the porosity only, could not determine the rate of adsorption accurately. It is advisable that the pore surface areas of the biomass are to be determined. Equipment suggested to be used is the BET which measured the average pore diameters and surface areas of an adsorbent. From the analysis, comparison and discussion could be made more effectively.

Existing adsorption process to adsorb benzene and toluene are known to used the commercialize granular activated carbons as the adsorbent. To see the effectiveness of removing these organic compounds using the *Pandanus amaryllifolius Roxb* leaves as an

adsorbent, a comparison should be done between the two adsorbent. Experiment using granular activated carbon replacing the *Pandanus amaryllifolius Roxb* leaves should be run. This would provide a better analysis in terms of comparison.

Lastly, the experiment was run to see the effect of pretreatment and drying towards the uptake. Each effect was being experimented individually. It is recommended that these effects were combined in obtaining an optimum rate of removals. Drying and pretreatment effect could be done altogether in a series of steps to obtain an optimum biomass to enhance the adsorption process.

REFERENCES

Books

Cary T. Chiou, 2002, "*Partition and Adsorption of Organic Contaminants in Environmental Systems*", United States of America, John Wiley & Sons

Geankoplis Christie J., 1993, "*Transport Process and Unit Operations*", Third Edition, New Jersey, Prentice Hall International, Inc.

Geoffrey A. Cordell, 2001, "*The Alkaloids*", Volume 57, United States of America, Academic Press

George Wypech, 2001, "*Handbooks of Solvents*", Toronto, New York, William Andrew Publishing and ChemTec Publishing

Hughes MN and Poole RK, 1989, "*Metals and Microorganisms*", London, Chapman and Hall

Legal Research Board, 2003, "*Environmental Quality Act 1974 (Act 127) & Subsidiary Legislation*", Selangor Darul Ehsan, International Law Book Services

Metcalf and Eddy, 2003, "*Wastewater Engineering Treatment and Reuse*", United States of America, McGraw-Hill

Robert C. Atkins and Francis A. Carey, 2002, "*Organic Chemistry, A Brief Course*", Third Edition, United States of America, McGraw-Hill

Robert M. Clark, Benjamin W.Lykins, Jr., 1989, "*Granular Activated Carbon: Design, Operation, and Cost*", United States of America, Lewis Publisher

Journals

Cancun, 1997, *"Flavor and Chemistry of Ethnic Foods"*, In Proceedings of a Meeting held during the 5th Chemical Congress of North America

C.A. Toles, W.E. Marshall and M.M. Johns, 1997, *"Granular Activated Carbons from Nutshells for the Uptake of Metals and Organic Compound"*, Chemical Engineering Science, Vol. 35, No. 9, pp. 1407-1414, 1997, Great Britain, Elsevier Science Ltd

Foster, NS, JW Day, RH Filby, A Alford, and D Rogers. 2002, *"The Role of Na-Montmorillonite in the Evolution of Copper, Nickel, and Vanadyl Geoporphyrins during Diagenesis." Organic Geochemistry* 33(8):907-919

Galun M, Galun E, Siedel BZ, Keller P, Lehr H and Siegel SM, 1987, *"Removal of metal ions from aqueous solutions by Penicillum biomass: Kinetic and uptake parameters". Water, Air and Soil Pollution* 33: 359-371

Guangyu Yan and T Viraraghavan, 2000, *"Effect of pretreatment on the bioadsorption of heavy metals on Mucor Rouxii"*, Water SA Vol. 26 No. 1

Hiromitsu Takayama, Tomotake Ichikawa, Mariko Kitajima, Norio Aimi, Dazy Lopezb and Maribel G. Nonatob, 2001, *"A new alkaloid, pandanamine;finding of an anticipated biogenetic intermediate Pandanus amaryllifolius Roxb"*, Tetrahedron Letters 42 (2001) 2995–2996, Great Britain, Elsevier Science Ltd.

Kristof Demeestere, Jo Dewuff, Herman Van Langenhove, Bram Sercu, 2002, *"Gas-Solid Adsorption of Selected Volatile Organic Compounds on Titanium Dioxide Degussa P25"*, Chemical Engineering Science, Great Britain, Elsevier Science Ltd

Whistler R and Daniel TR, 1985, *"Carbonhydrates"*, In: Owen R Fennema (ed.) Food Chemistry : 96-105

Websites

<http://www.chem.vt.edu>

<http://www.emsl.pnl.gov/capabs/ri/uv_vis.shtml>

<http://www.friedli.com/herbs/phytochem/alkaloids.gif>

Tony Reeder, 2004 <http://www.chem.biomedchem.uwa.edu.au/page/39662>

APPENDICES

Appendix A: Maximum Contamination Limit and Sample Calculations

Table A.1: Maximum Contamination Limit

Appendix B: UV-Vis Analysis of Benzene

Appendix C: UV-Vis Analysis of Toluene

Appendix D: Standard Calibration Curve of Toluene

Appendix A

Table A.1: Maximum Contamination Limit

Organic Compound	Maximum Contamination Limit (mg/L)
Benzene	0.005
Toluene	1.0

Sample Calculations

1. Preparation of 5ppm Benzene Solution

1ppm = 1mg of benzene / L of distill water

MW of Benzene = 78.11g/mol

Density of Benzene = $C_1/C_2^{[1+(1-T/C3)C4]}$

At T = 298K

$C_1 = 1.0162$

$C_2 = 0.2655$

$C_3 = 562.16$

$C_4 = 0.28212$

Density of Benzene = 0.873 g/cm^3 = 0.873 g/mL

Solubility of benzene = 0.07 = 700ppm = 700mg/L

Mass = 700mg = 0.7 g

Volume = mass / density

= 0.7g / 0.873 g/mL

= 0.80mL

To make 700ppm benzene solution, needs **0.8 mL** of pure benzene.

$V_1C_1 = V_2C_2$

V_1 x 700ppm = 1000mL x 5ppm

$V_1 = 7.14$ mL

Thus, to make 5ppm of benzene solution needs **7.14mL** of 700ppm benzene solution.

2. Preparation of 5ppm Toluene Solution

1ppm = 1mg of toluene / L of distill water

MW of toluene = 92.13g/mol

Density of toluene = $C_1/C_2^{[1+(1-T/C3)C4]}$

At T = 298K

$C_1 = 0.8488$

$C_2 = 0.26655$

$C_3 = 591.8$

$C_4 = 0.2878$

Density of toluene = 0.865 g/cm^3 = 0.865 g/mL

Solubility of toluene = 0.05 = 500ppm = 500mg/L

Mass = 500mg = 0.5 g

Volume = mass / density

= 0.5 g / 0.865 g/mL

= 0.578mL

To make 500ppm toluene solution, needs **0.578mL** of pure toluene.

$V_1C_1 = V_2C_2$

V_1 x 500ppm = 1000mL x 5ppm

V_1 = 10mL

Thus, to make 5ppm of toluene solution needs **10mL** of 500ppm toluene solution.

3. Preparation of 0.1M Sodium Hydroxide (NaOH)

MW of NaOH = 40g/mol

Volume = 250mL

Mass = 0.1 mol/L x 40g/mol x 0.25L

= 1g

To make 250mL of 0.1M NaOH, a mass of 1g NaOH are diluted in distill water.

4. Preparation of 0.1M Hydrochloric Acid (HCL)

MW of 37% HCL = 36.46 g/mol

Sg of HCL = 1.19 kg/L

$M_1V_1 = M_2V_2$

$1/M_1$ = 36.46g/mol x 1L/1.19kg x 1kg/1000g

= 0.03064

M_1 = 32.64 mol/L

M_2 = 0.1 mol/L

V_2 = 0.5 L

V_1 = (0.1 mol/L x 0.5L)/ 32.64 mol/L

= 1.53×10^{-3}L = 1.53mL

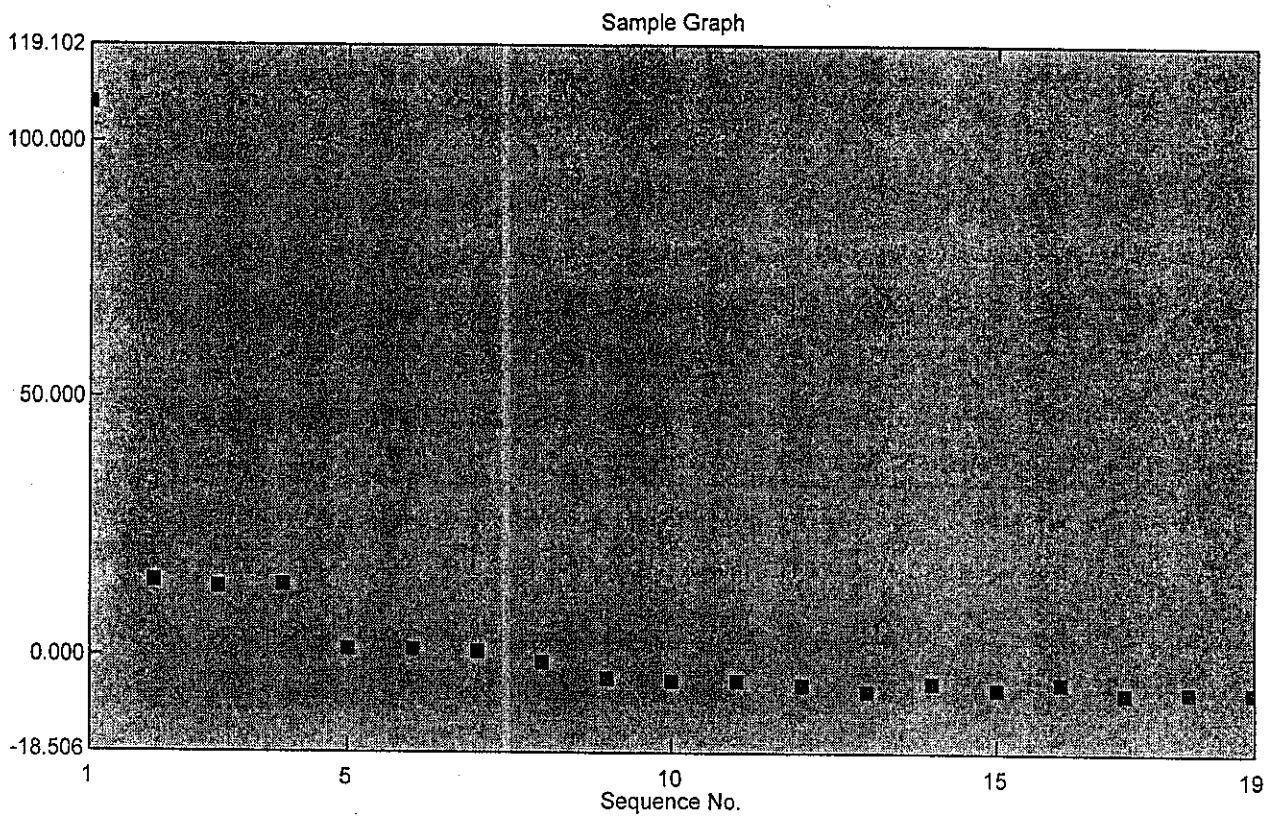
To make 500mL of 0.1M HCL, 1.53mL of HCL need to be diluted with distill water.

Appendix B: UV-Vis Analysis of Benzene

ımple Table Report

10/12/2004 11:02:05 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzeneRAW.pho



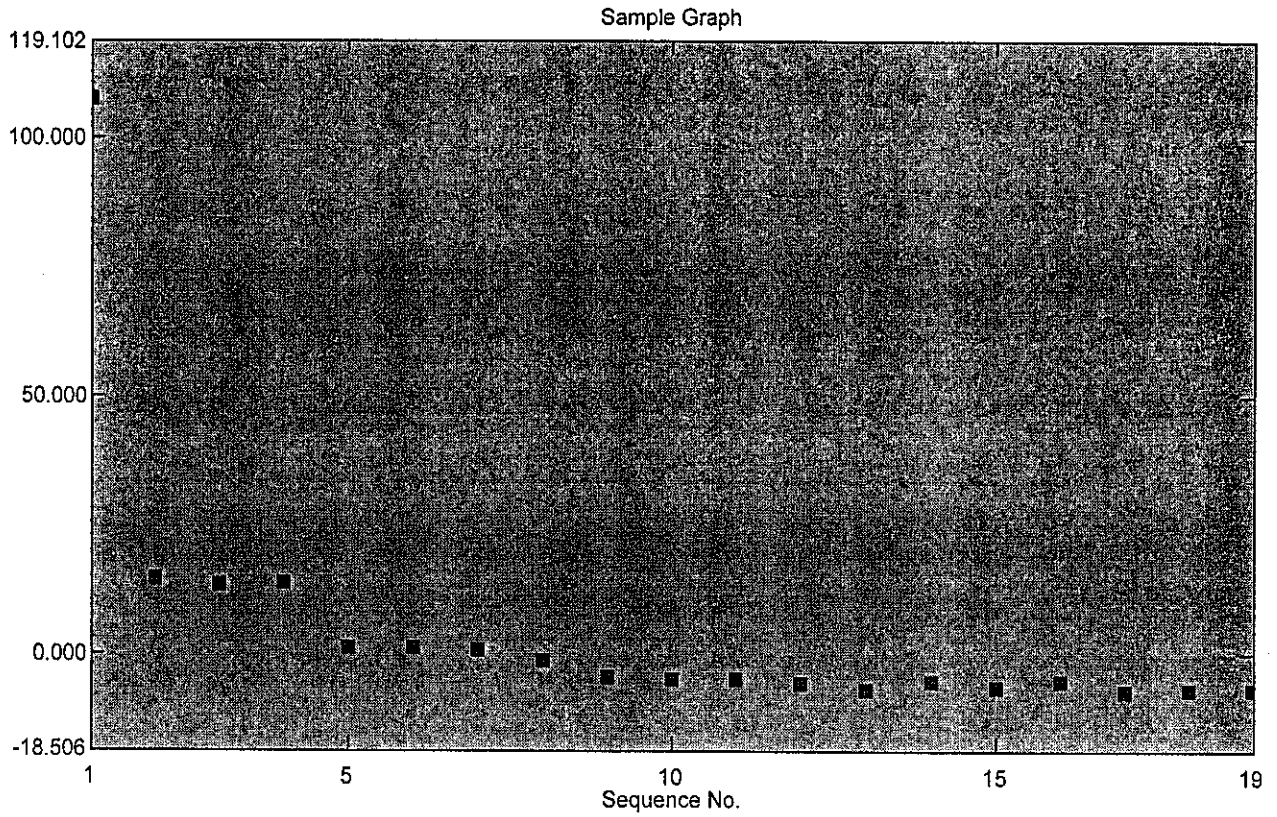
e Table

	Sample ID	Type	Ex	Conc	WL200.0	Comments
	sample1_0	Unknown		107.634	5.000	
	sample2_5	Unknown		14.643	1.013	
	sample3_10	Unknown		13.406	0.960	
	sample4_15*	Unknown		13.840	0.979	
	sample5_20	Unknown		1.413	0.446	
	sample6_25	Unknown		1.451	0.448	
	sample7_30	Unknown		1.015	0.429	
	sample8_45	Unknown		-1.049	0.341	
	sample9_60	Unknown		-4.429	0.196	
	sample10_75	Unknown		-4.889	0.176	
	sample11_90	Unknown		-4.871	0.177	
	sample12_10	Unknown		-5.718	0.141	
	sample13_12	Unknown		-6.745	0.097	
	sample14_13	Unknown		-5.390	0.155	
	sample15_15	Unknown		-6.224	0.119	
	sample16_16	Unknown		-5.129	0.166	
	sample17_18	Unknown		-7.039	0.084	
	sample18_21	Unknown		-6.979	0.087	

ımple Table Report

10/12/2004 11:02:05 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzeneRAW.pho



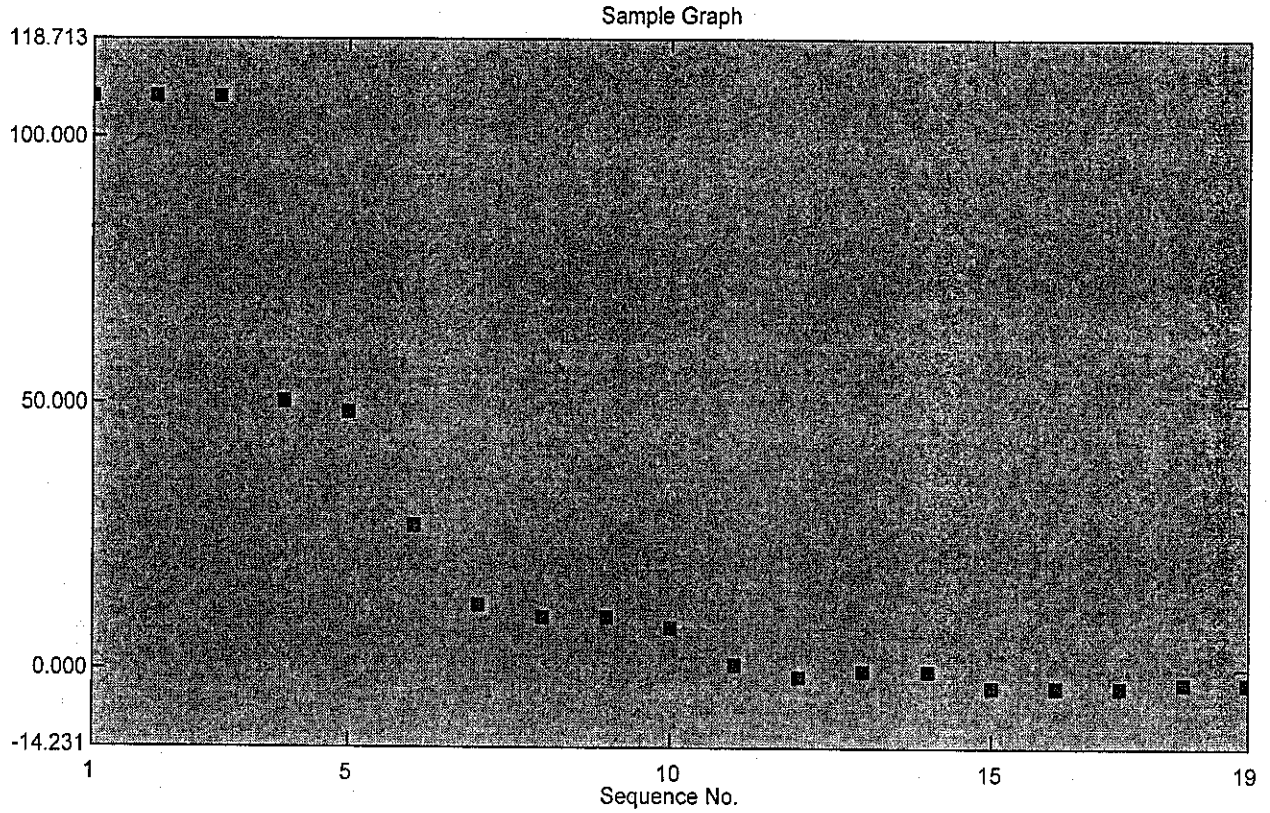
e Table

	Sample ID	Type	Ex	Conc	WL200.0	Comments
	sample19_24	Unknown		-6.993	0.086	

ample Table Report

10/12/2004 10:49:25 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzeneHCL.pho



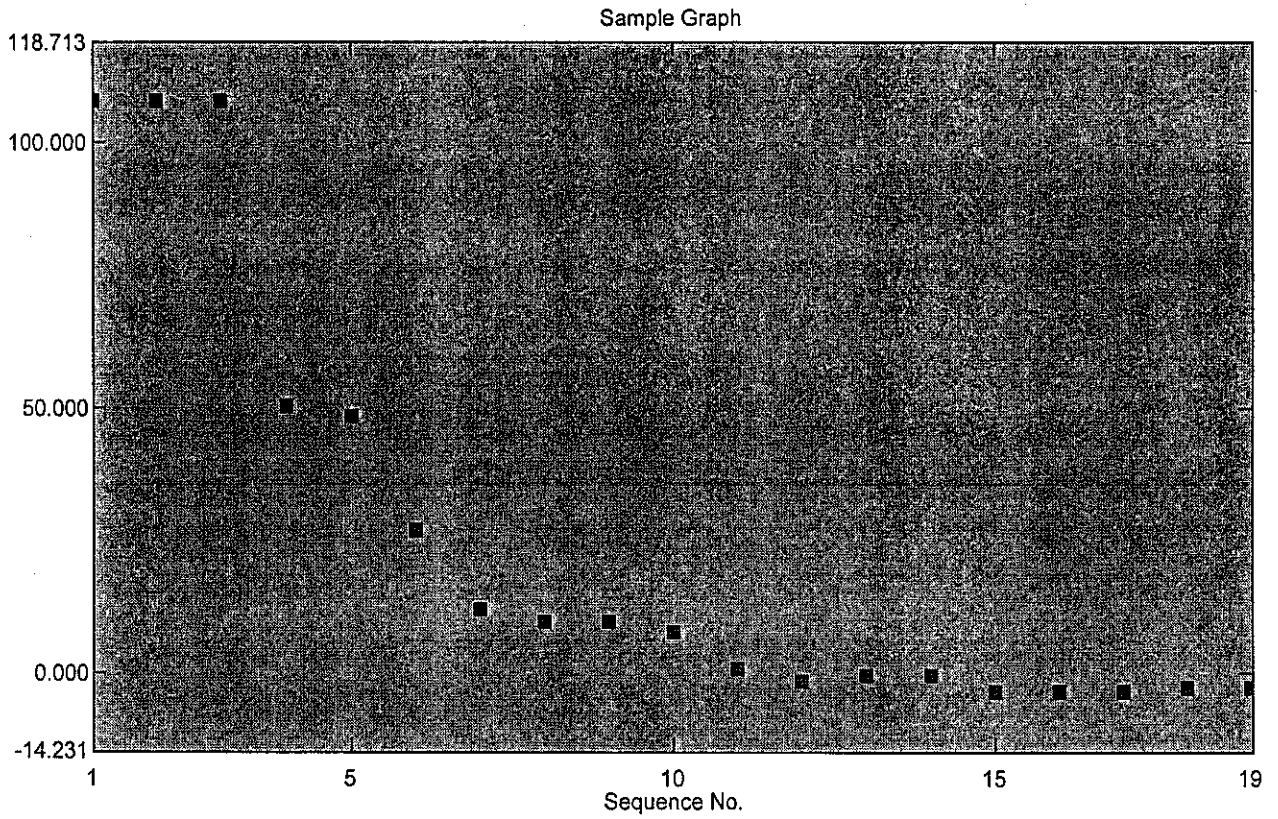
e Table

Sample ID	Type	Ex	Conc	WL200.0	Comments
sample1_0	Unknown		107.634	5.000	
sample2_5	Unknown		107.634	5.000	
sample3_10	Unknown		107.634	5.000	
sample4_15	Unknown		50.314	2.543	
sample5_20	Unknown		48.350	2.458	
sample6_25	Unknown		27.051	1.545	
sample7_30	Unknown		12.432	0.919	
sample8_45	Unknown		9.759	0.804	
sample9_60	Unknown		9.897	0.810	
sample10_75	Unknown		8.008	0.729	
sample11_90	Unknown		1.059	0.431	
sample12_10	Unknown		-1.173	0.335	
sample13_12	Unknown		-0.186	0.378	
sample14_13	Unknown		-0.188	0.378	
sample15_15	Unknown		-3.136	0.251	
sample16_16	Unknown		-3.147	0.251	
sample17_18	Unknown		-3.152	0.251	
sample18_21	Unknown		-2.406	0.283	

ımple Table Report

10/12/2004 10:49:25 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzeneHCL.pho



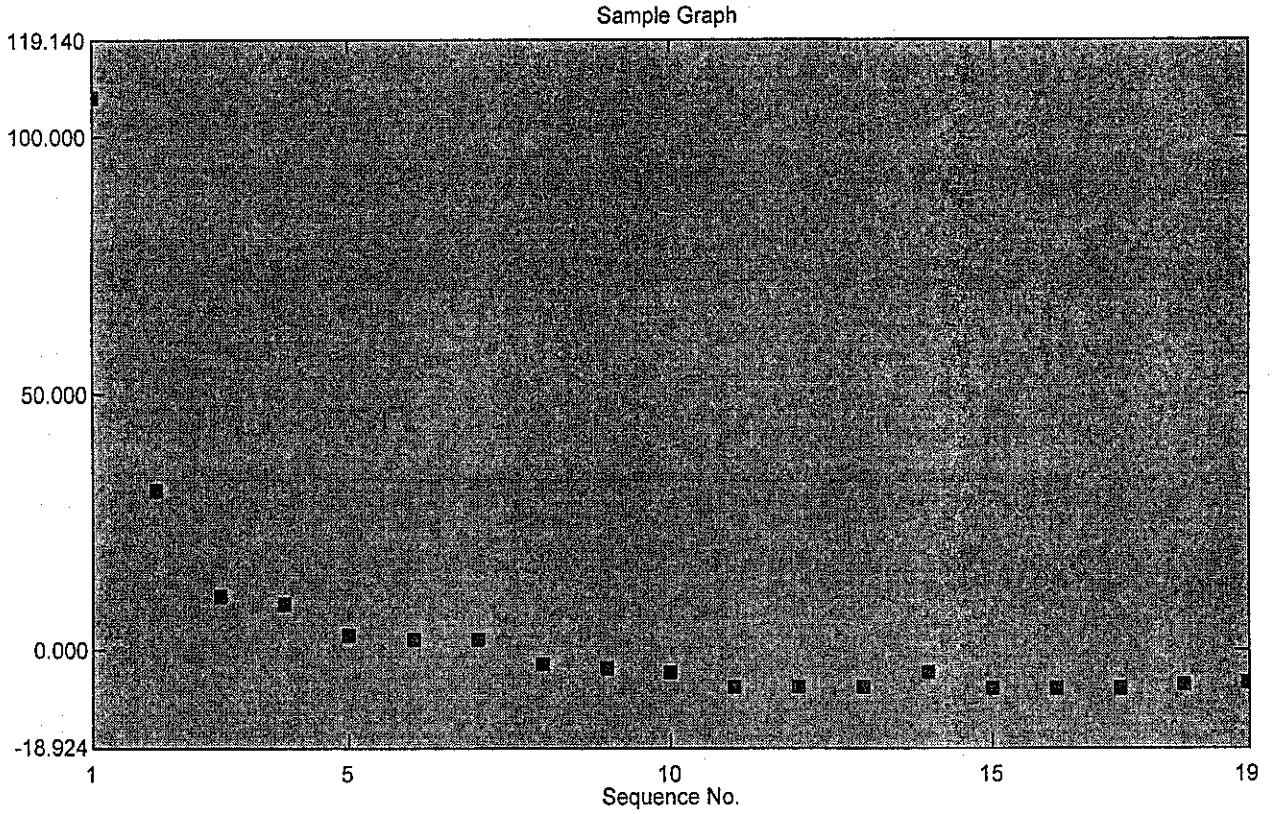
le Table

	Sample ID	Type	Ex	Conc	WL200.0	Comments
	sample19_24	Unknown		-2.411	0.282	

mple Table Report

10/12/2004 10:56:50 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzeneNaOH.pho



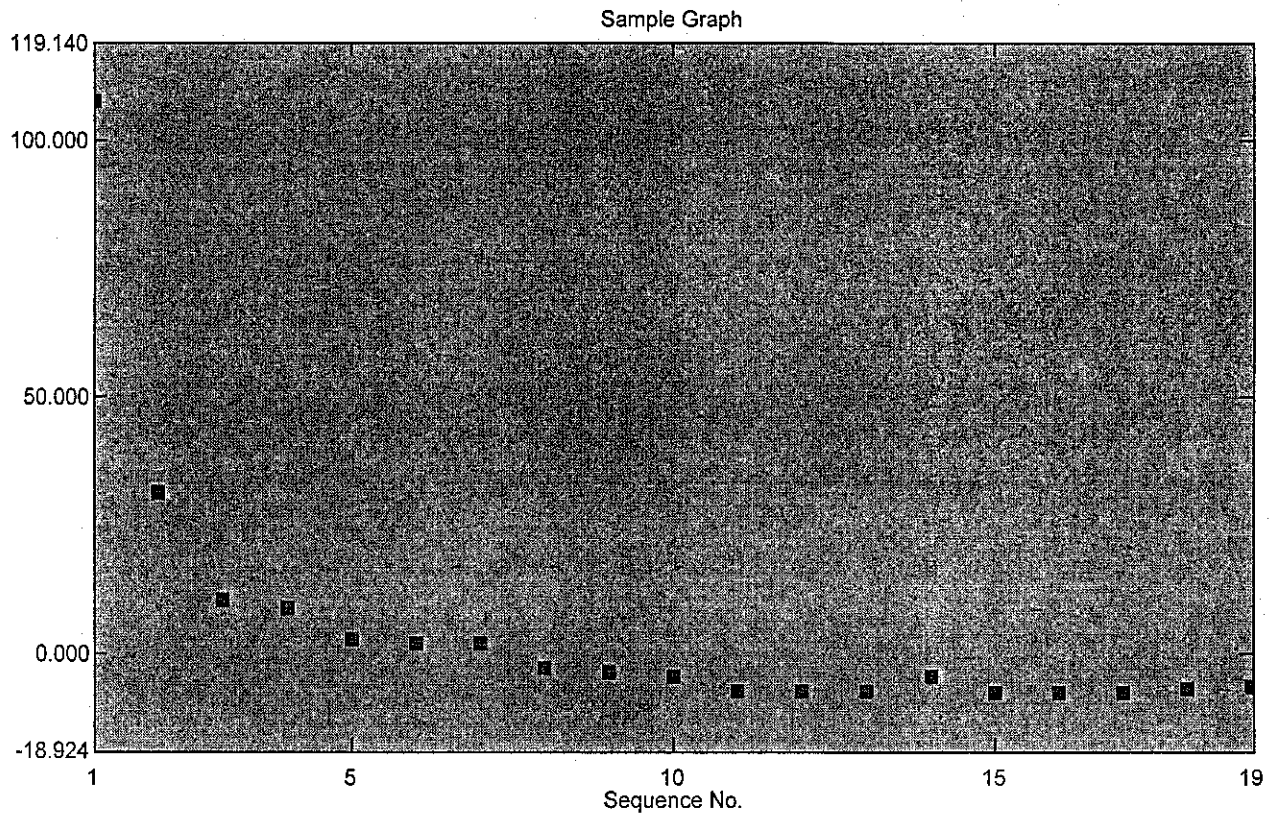
e Table

Sample ID	Type	Ex	Conc	WL200.0	Comments
sample1_0	Unknown		107.634	5.000	
sample2_5	Unknown		31.109	1.719	
sample3_10	Unknown		10.820	0.850	
sample4_15	Unknown		8.933	0.769	
sample5_20	Unknown		2.789	0.505	
sample6_25	Unknown		2.005	0.472	
sample7_30	Unknown		1.969	0.470	
sample8_45	Unknown		-2.663	0.272	
sample9_60	Unknown		-3.727	0.226	
sample10_75	Unknown		-4.433	0.196	
sample11_90	Unknown		-7.045	0.084	
sample12_10	Unknown		-7.127	0.080	
sample13_12	Unknown		-7.188	0.078	
sample14_13	Unknown		-4.403	0.197	
sample15_15	Unknown		-7.402	0.068	
sample16_16	Unknown		-7.416	0.068	
sample17_18	Unknown		-7.419	0.068	
sample18_21	Unknown		-6.634	0.101	

mple Table Report

10/12/2004 10:56:50 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzeneNaOH.pho



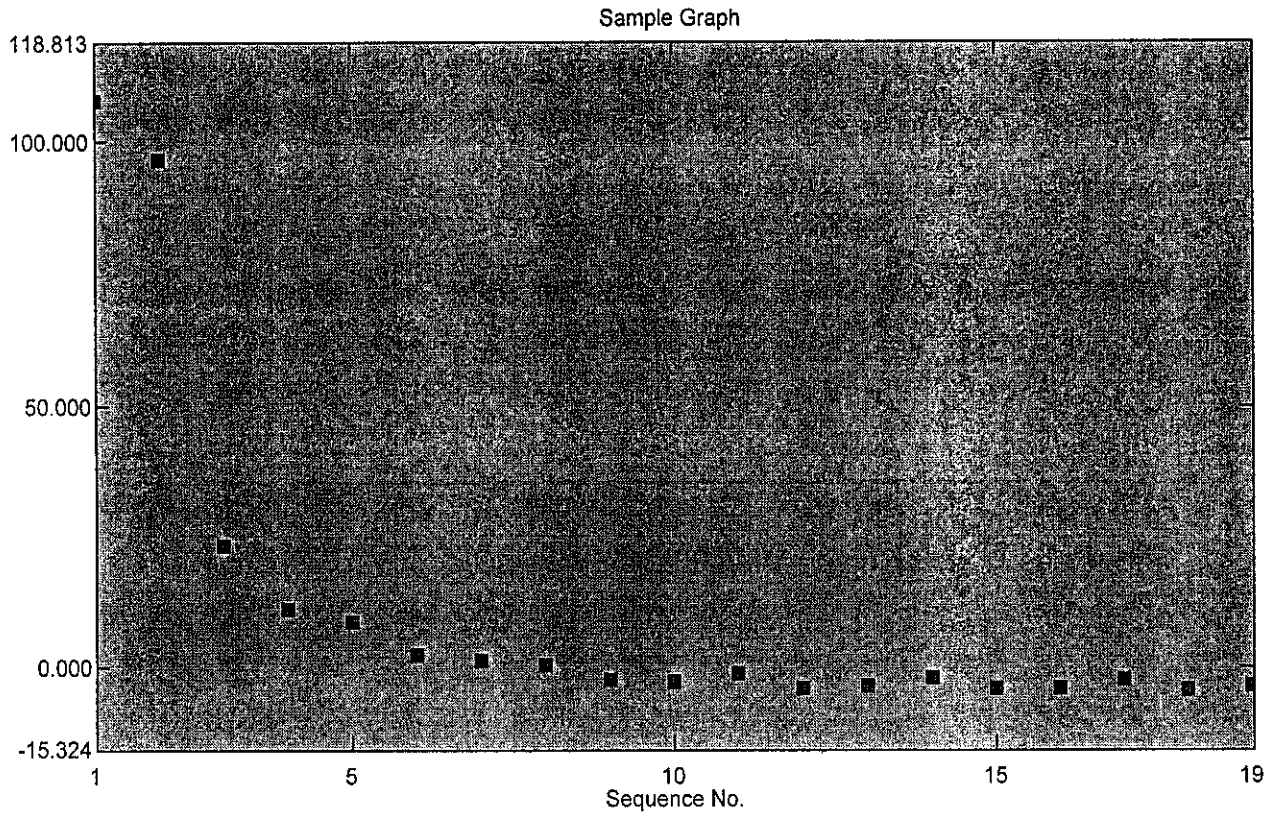
e Table

	Sample ID	Type	Ex	Conc	WL200.0	Comments
	sample19_24	Unknown		-6.546	0.105	

ımple Table Report

10/12/2004 10:41:50 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzene50.pho



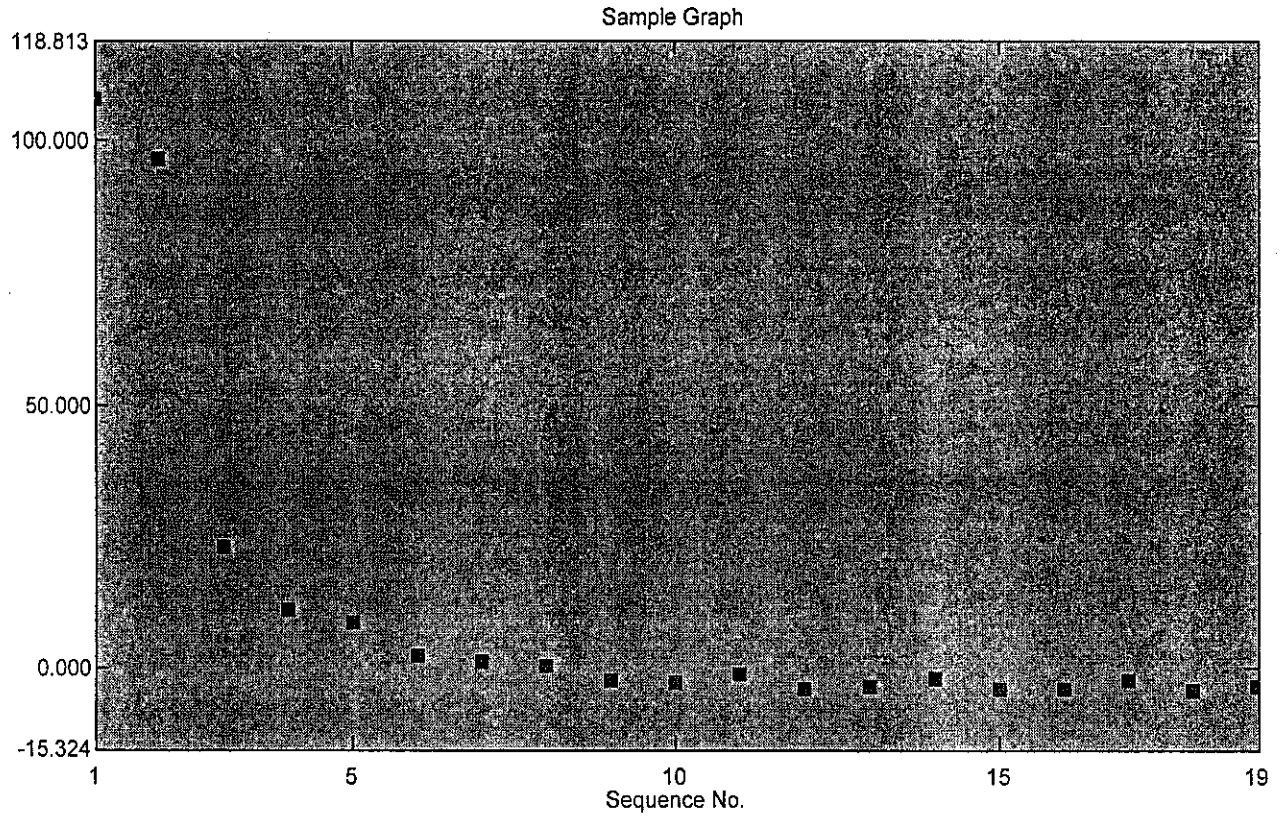
le Table

	Sample ID	Type	Ex	Conc	WL200.0	Comments
	sample1_0	Unknown		107.634	5.000	
	sample2_5	Unknown		96.351	4.516	
	sample3_10	Unknown		23.382	1.388	
	sample4_15	Unknown		10.909	0.853	
	sample5_20	Unknown		8.700	0.759	
	sample6_25	Unknown		2.312	0.485	
	sample7_30	Unknown		1.309	0.442	
	sample8_45	Unknown		0.532	0.409	
	sample9_60	Unknown		-2.518	0.278	
	sample10_75	Unknown		-2.713	0.269	
	sample11_90	Unknown		-1.249	0.332	
	sample12_10	Unknown		-3.865	0.220	
	sample13_12	Unknown		-3.407	0.240	
	sample14_13	Unknown		-2.049	0.298	
	sample15_15	Unknown		-3.932	0.217	
	sample16_16	Unknown		-3.871	0.220	
	sample17_18	Unknown		-2.172	0.293	
	sample18_21	Unknown		-4.146	0.208	

ımple Table Report

10/12/2004 10:41:50 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzene50.pho



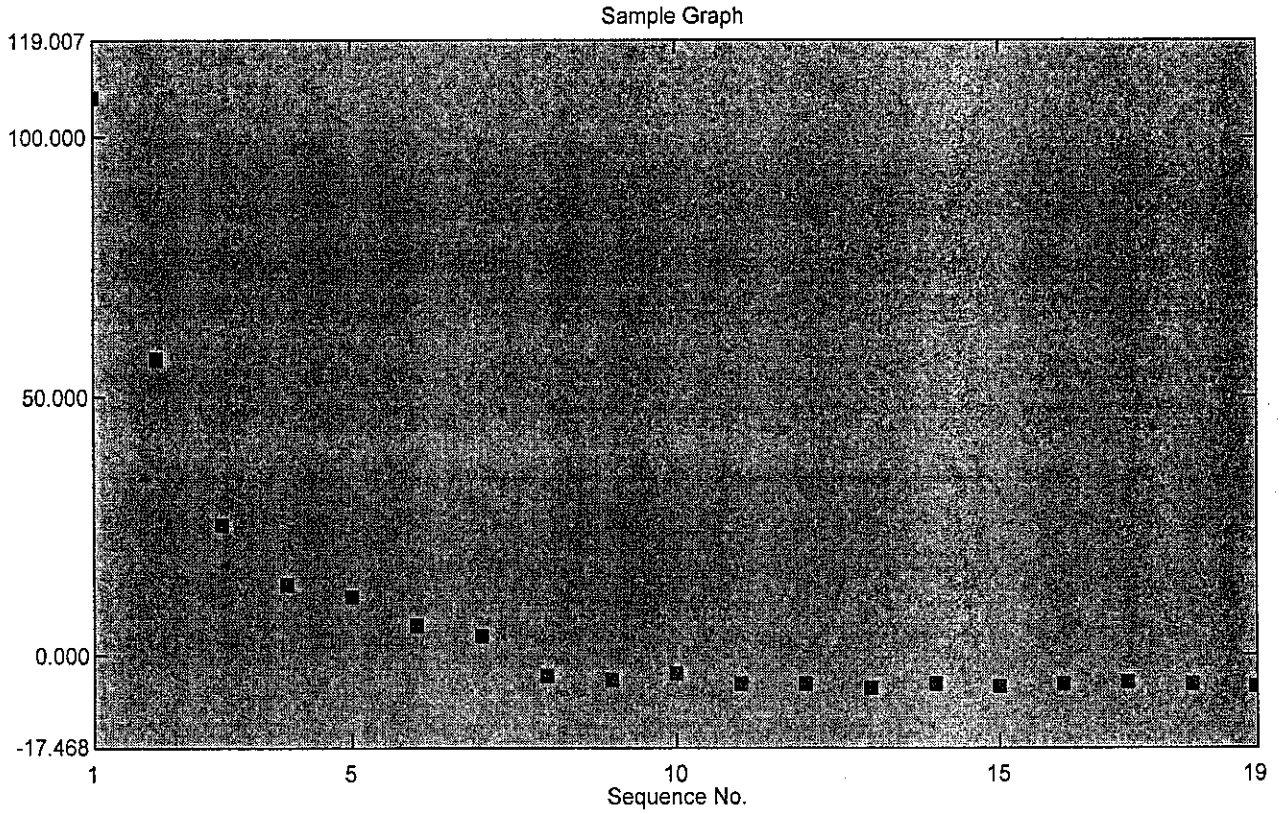
le Table

	Sample ID	Type	Ex	Conc	WL200.0	Comments
	sample19_24	Unknown		-3.375	0.241	

mple Table Report

10/12/2004 10:43:13 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzene80.pho



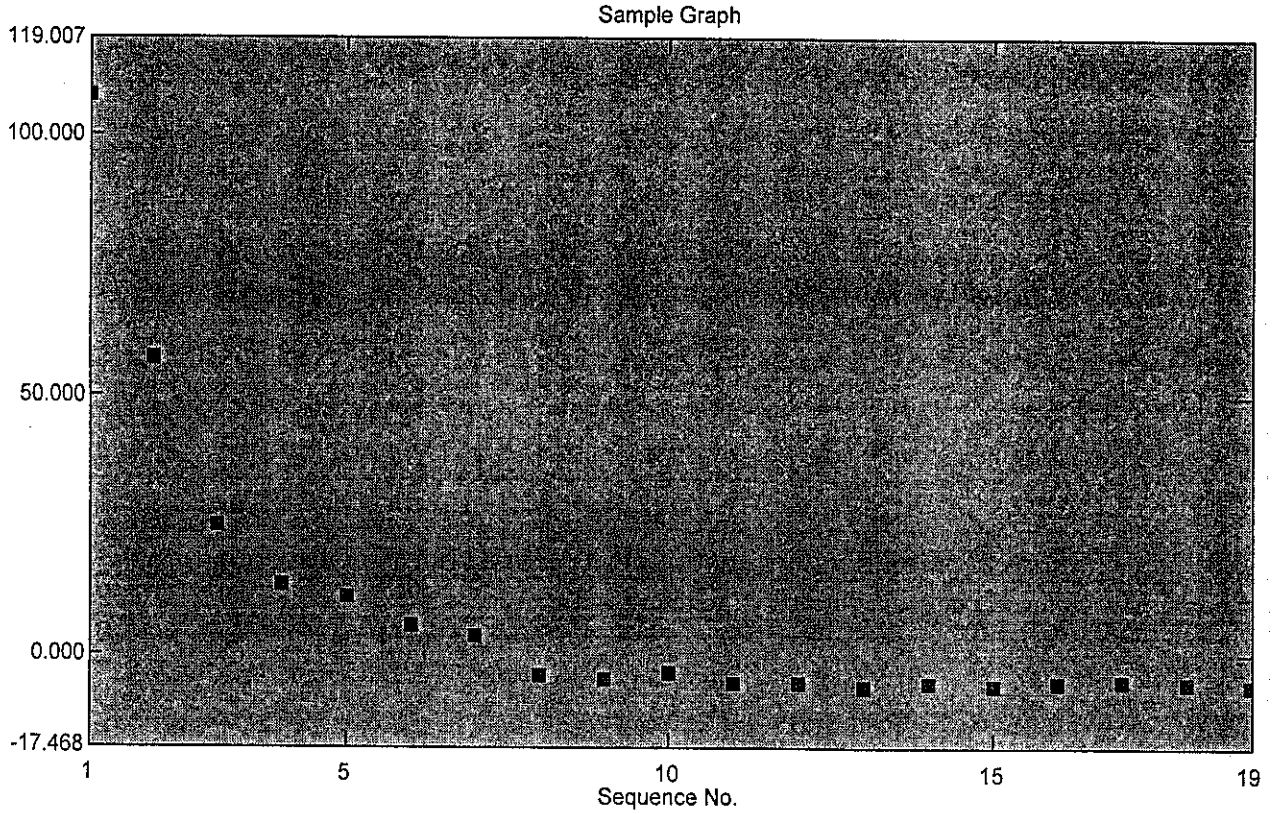
e Table

Sample ID	Type	Ex	Conc	WL200.0	Comments
sample1_0	Unknown		107.634	5.000	
sample2_5	Unknown		57.228	2.839	
sample3_10	Unknown		25.354	1.473	
sample4_15	Unknown		13.742	0.975	
sample5_20	Unknown		11.501	0.879	
sample6_25	Unknown		5.808	0.635	
sample7_30	Unknown		3.912	0.553	
sample8_45	Unknown		-3.842	0.221	
sample9_60	Unknown		-4.584	0.189	
sample10_75	Unknown		-3.607	0.231	
sample11_90	Unknown		-5.619	0.145	
sample12_10	Unknown		-5.501	0.150	
sample13_12	Unknown		-6.095	0.124	
sample14_13	Unknown		-5.528	0.149	
sample15_15	Unknown		-5.922	0.132	
sample16_16	Unknown		-5.522	0.149	
sample17_18	Unknown		-5.144	0.165	
sample18_19	Unknown		-5.273	0.160	

ample Table Report

10/12/2004 10:43:13 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzene80.pho



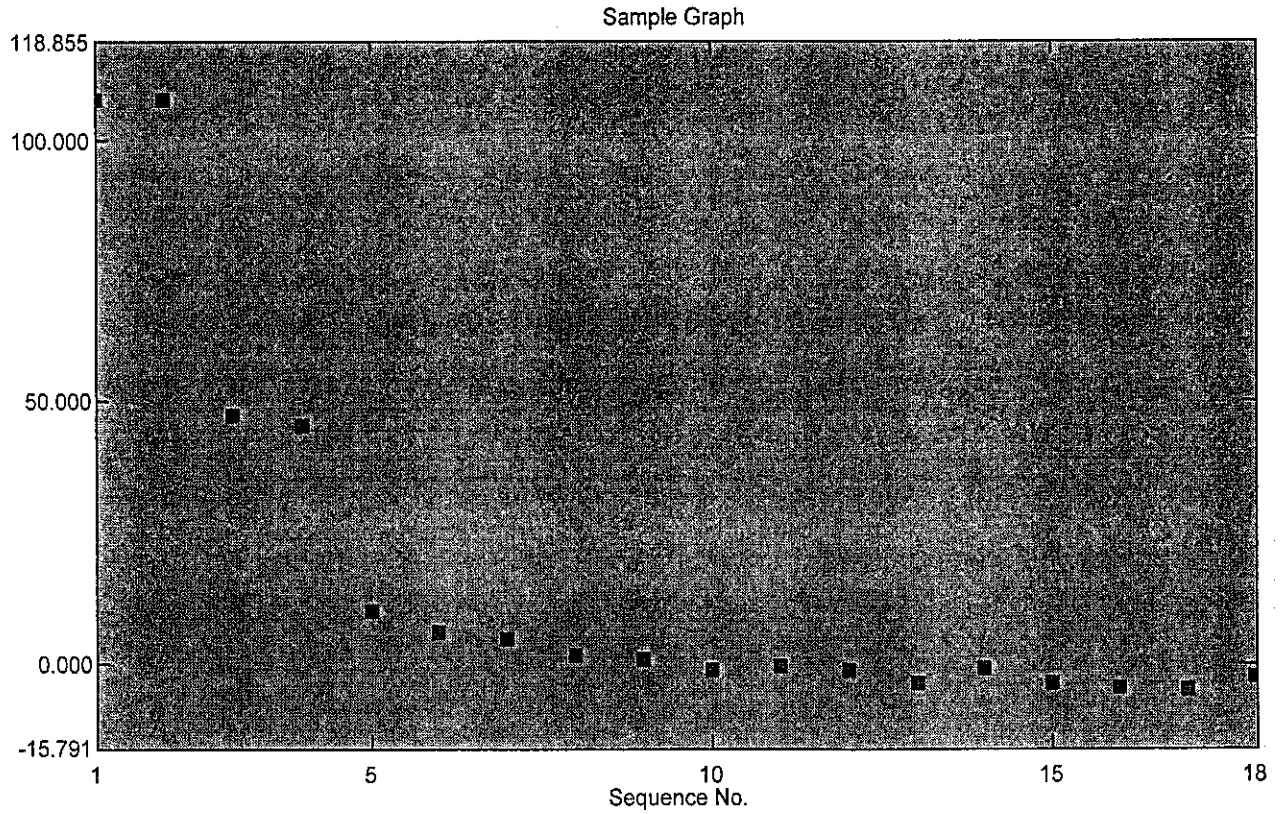
e Table

	Sample ID	Type	Ex	Conc	WL200.0	Comments
	sample19_21	Unknown		-6.044	0.127	

ımple Table Report

10/12/2004 10:45:22 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzene120.pho



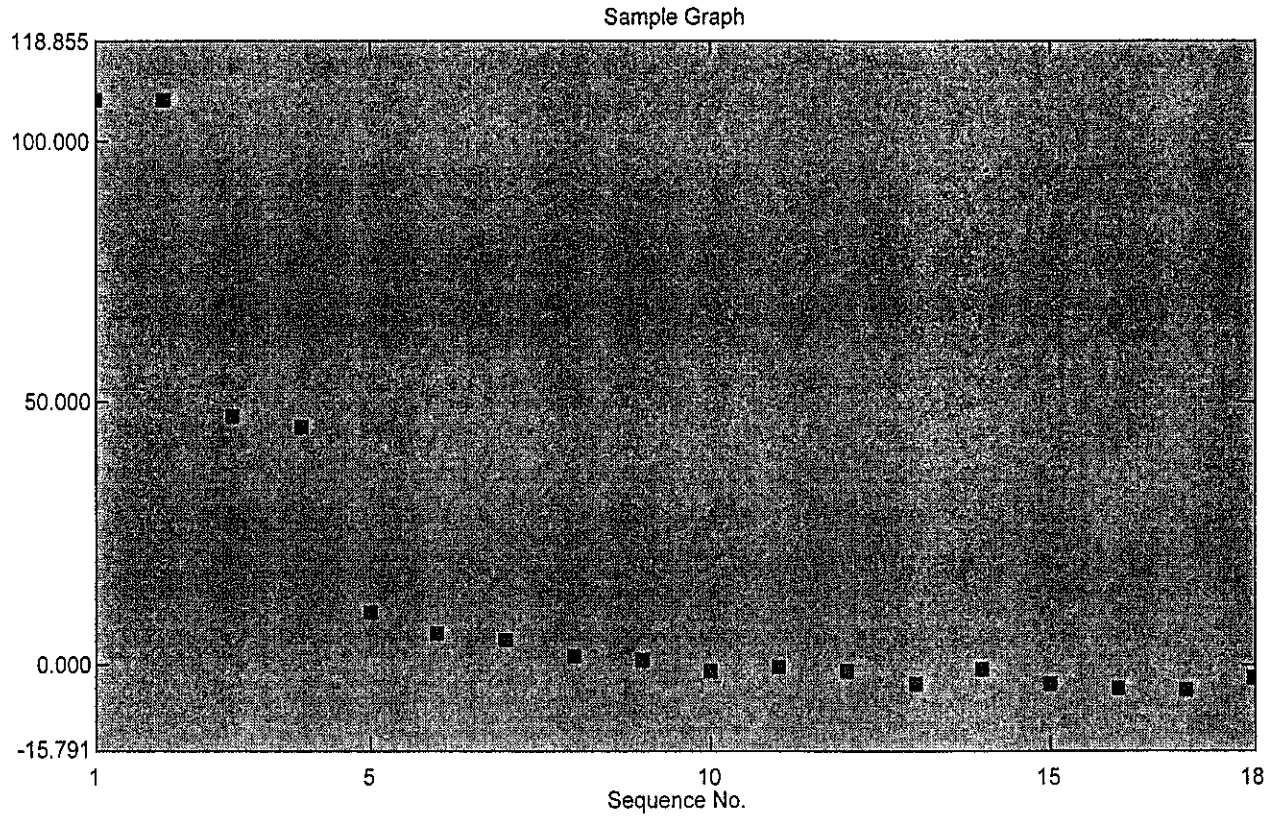
le Table

Sample ID	Type	Ex	Conc	WL200.0	Comments
sample1_0	Unknown		107.634	5.000	
sample2_5	Unknown		107.634	5.000	
sample3_10	Unknown		47.425	2.419	
sample4_15	Unknown		45.427	2.333	
sample5_20	Unknown		10.026	0.816	
sample6_25	Unknown		6.118	0.648	
sample7_30	Unknown		4.639	0.585	
sample8_45	Unknown		1.576	0.453	
sample9_60	Unknown		0.726	0.417	
sample10_75	Unknown		-1.318	0.329	
sample11_90	Unknown		-0.343	0.371	
sample12_10	Unknown		-1.124	0.338	
sample13_12	Unknown		-3.374	0.241	
sample14_13	Unknown		-0.861	0.349	
sample15_15	Unknown		-3.694	0.227	
sample16_16	Unknown		-4.327	0.200	
sample17_18	Unknown		-4.571	0.190	
sample18_21	Unknown		-2.366	0.284	

ample Table Report

10/12/2004 10:45:22 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\samplebenzene120.pho



le Table

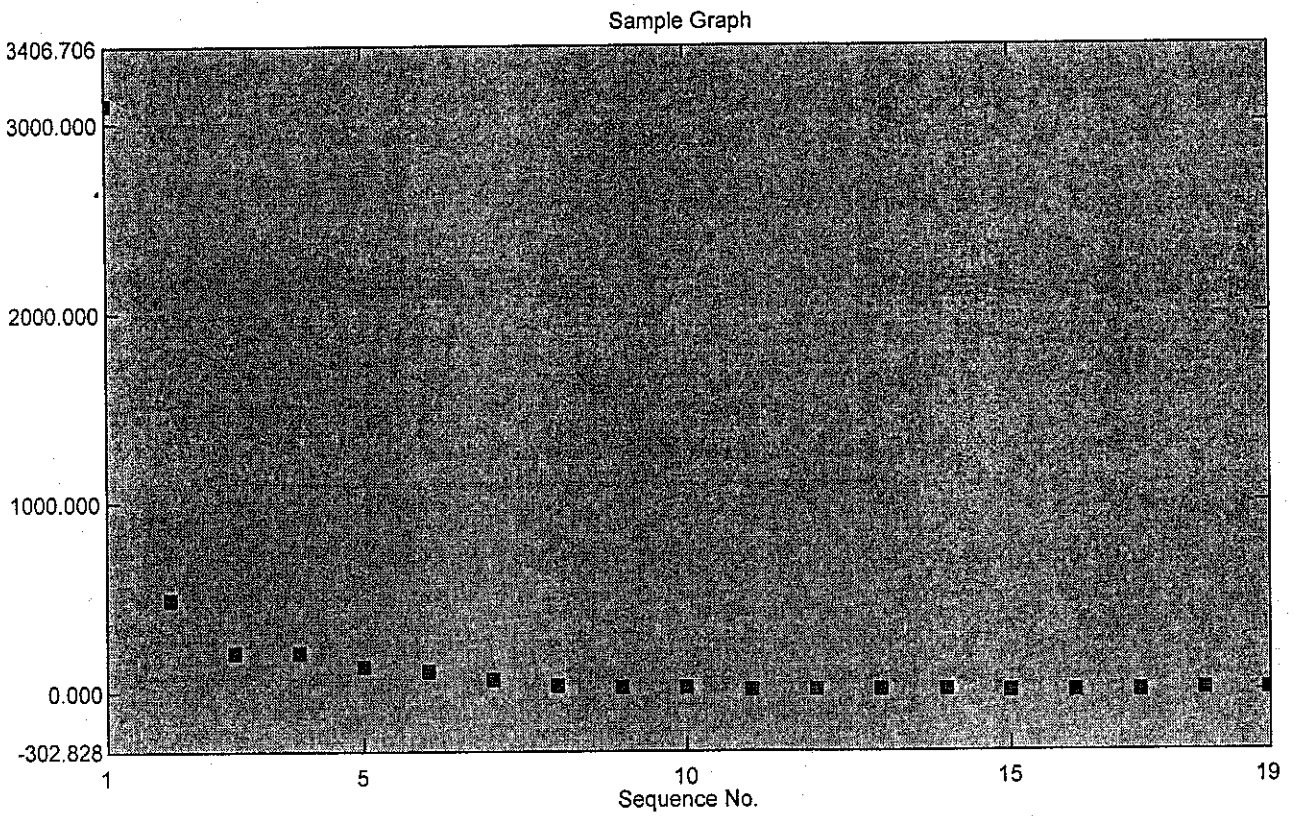
	Sample ID	Type	Ex	Conc	WL200.0	Comments

Appendix C: UV-Vis Analysis of Toluene

mple Table Report

10/12/2004 10:39:36 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletolueneRAW.pho



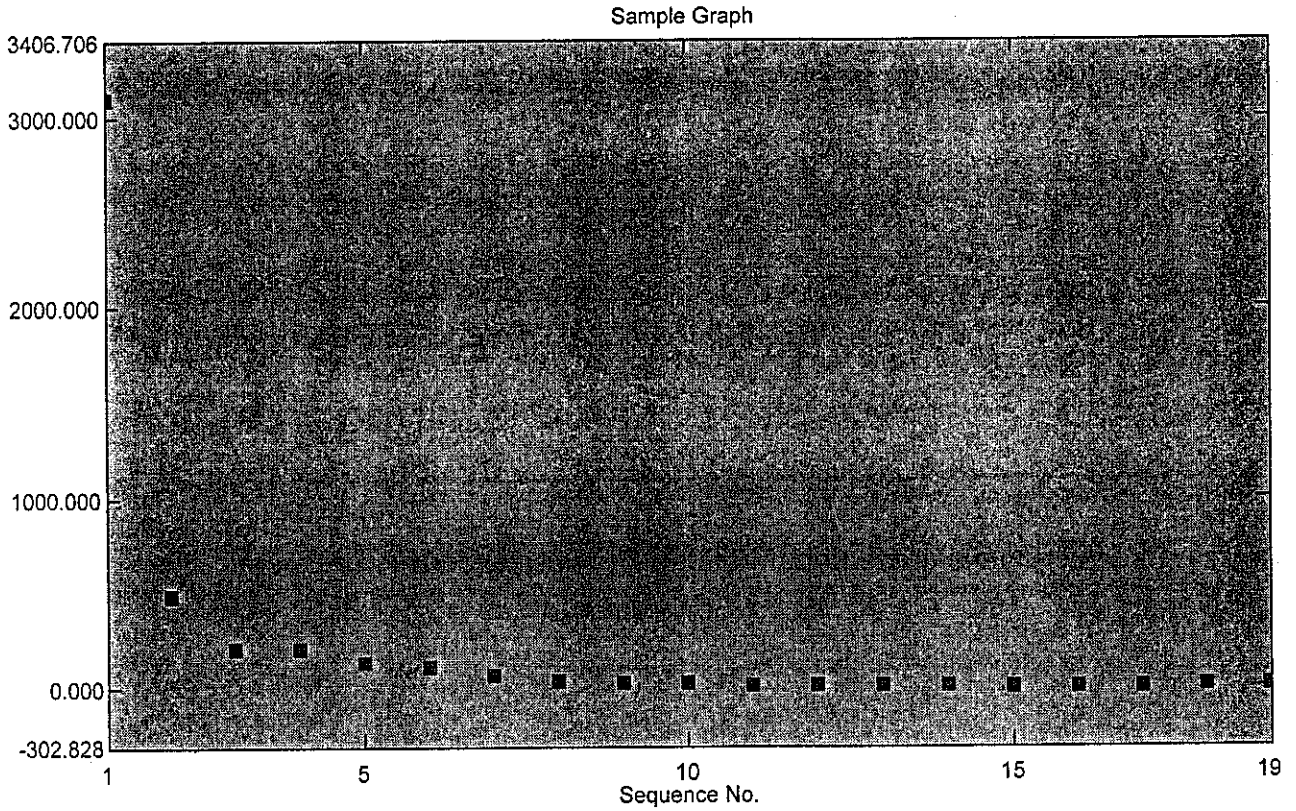
e Table

	Sample ID	Type	Ex	Conc	WL261.8	Comments
	sample1_0	Unknown		3097.579	5.000	
	sample2_5	Unknown		490.485	0.816	
	sample3_10	Unknown		204.428	0.357	
	sample4_15	Unknown		203.981	0.356	
	sample5_20	Unknown		129.303	0.236	
	sample6_25	Unknown		111.201	0.207	
	sample7_30	Unknown		66.480	0.135	
	sample8_45	Unknown		38.814	0.091	
	sample9_60	Unknown		22.852	0.065	
	sample10_75	Unknown		22.367	0.064	
	sample11_90	Unknown		13.887	0.051	
	sample12_10	Unknown		11.282	0.047	
	sample13_12	Unknown		11.672	0.047	
	sample14_13	Unknown		11.615	0.047	
	sample15_15	Unknown		6.804	0.039	
	sample16_16	Unknown		6.681	0.039	
	sample17_18	Unknown		6.300	0.039	
	sample18_21	Unknown		7.242	0.040	

mple Table Report

10/12/2004 10:39:36 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletolueneRAW.pho



e Table

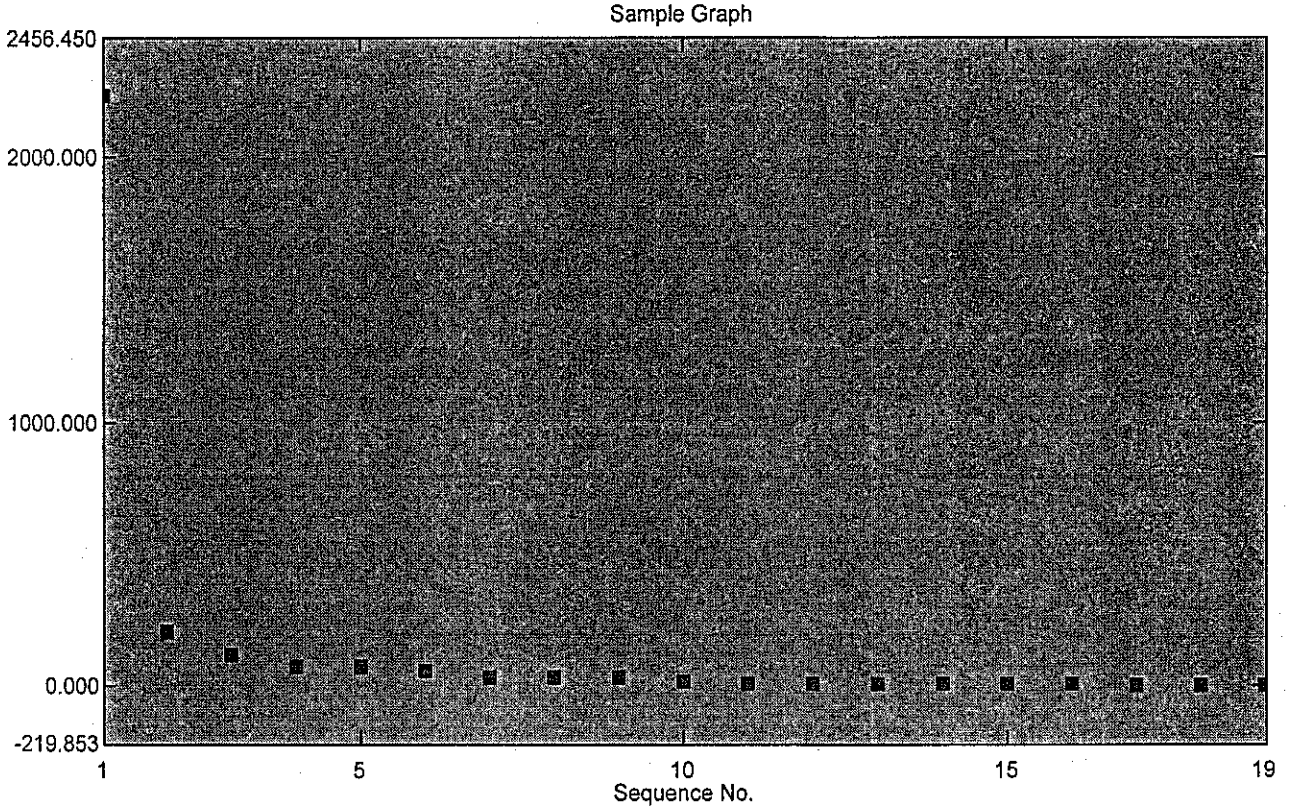
	Sample ID	Type	Ex	Conc	WL261.8	Comments
	sample19_24	Unknown		7.280	0.040	

mple Table Report

10/12/2004 09:48:42 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletolueneHCL.pho

Sample Graph



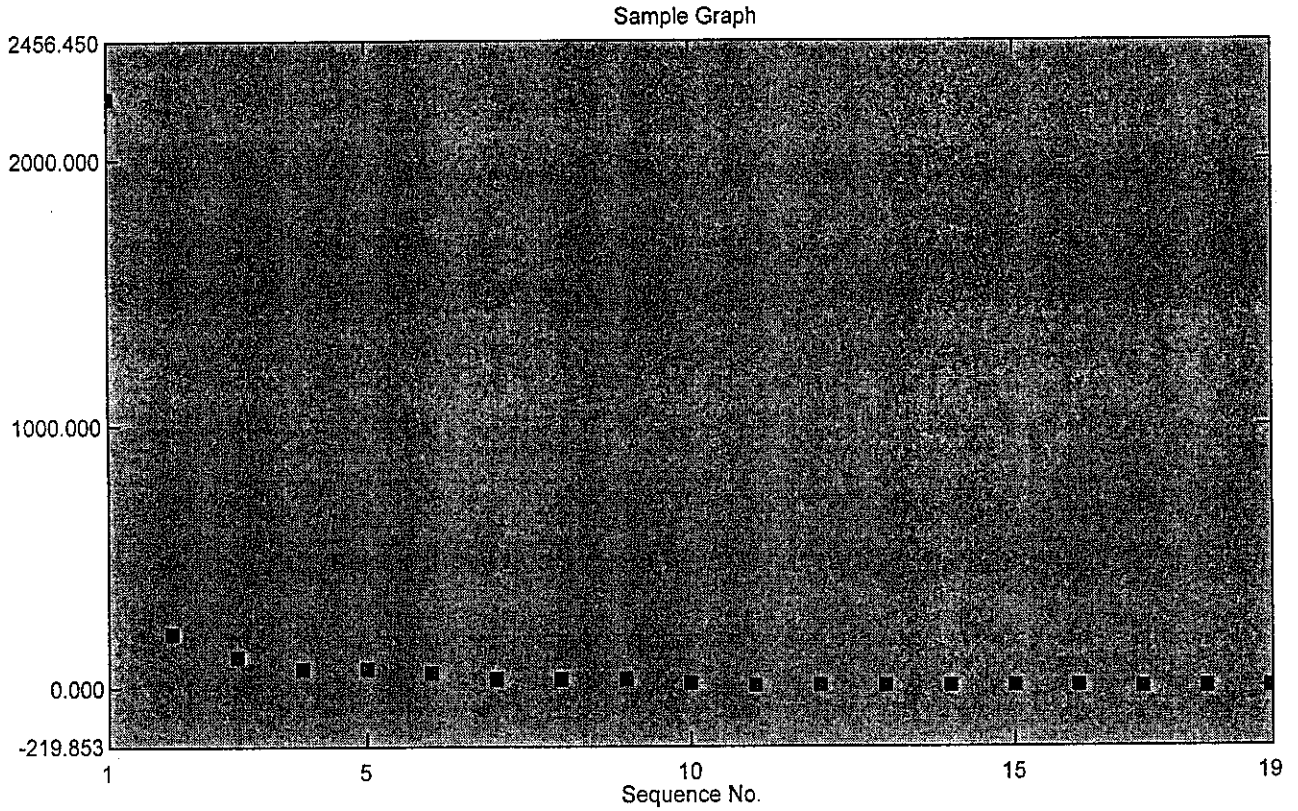
e Table

Sample ID	Type	Ex	Conc	WL261.8	Comments
sample1_0	Unknown		2233.425	3.613	
sample2_5	Unknown		205.017	0.357	
sample3_10	Unknown		114.234	0.212	
sample4_15	Unknown		68.543	0.138	
sample5_20	Unknown		68.296	0.138	
sample6_25	Unknown		58.095	0.122	
sample7_30	Unknown		34.869	0.084	
sample8_45	Unknown		34.213	0.083	
sample9_60	Unknown		34.232	0.083	
sample10_75	Unknown		15.009	0.052	
sample11_90	Unknown		7.470	0.040	
sample12_10	Unknown		6.443	0.039	
sample13_12	Unknown		5.074	0.037	
sample14_13	Unknown		4.732	0.036	
sample15_15	Unknown		5.749	0.038	
sample16_16	Unknown		5.673	0.038	
sample17_18	Unknown		3.173	0.033	
sample18_21	Unknown		3.429	0.034	

mple Table Report

10/12/2004 09:48:43 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletolueneHCL.pho



le Table

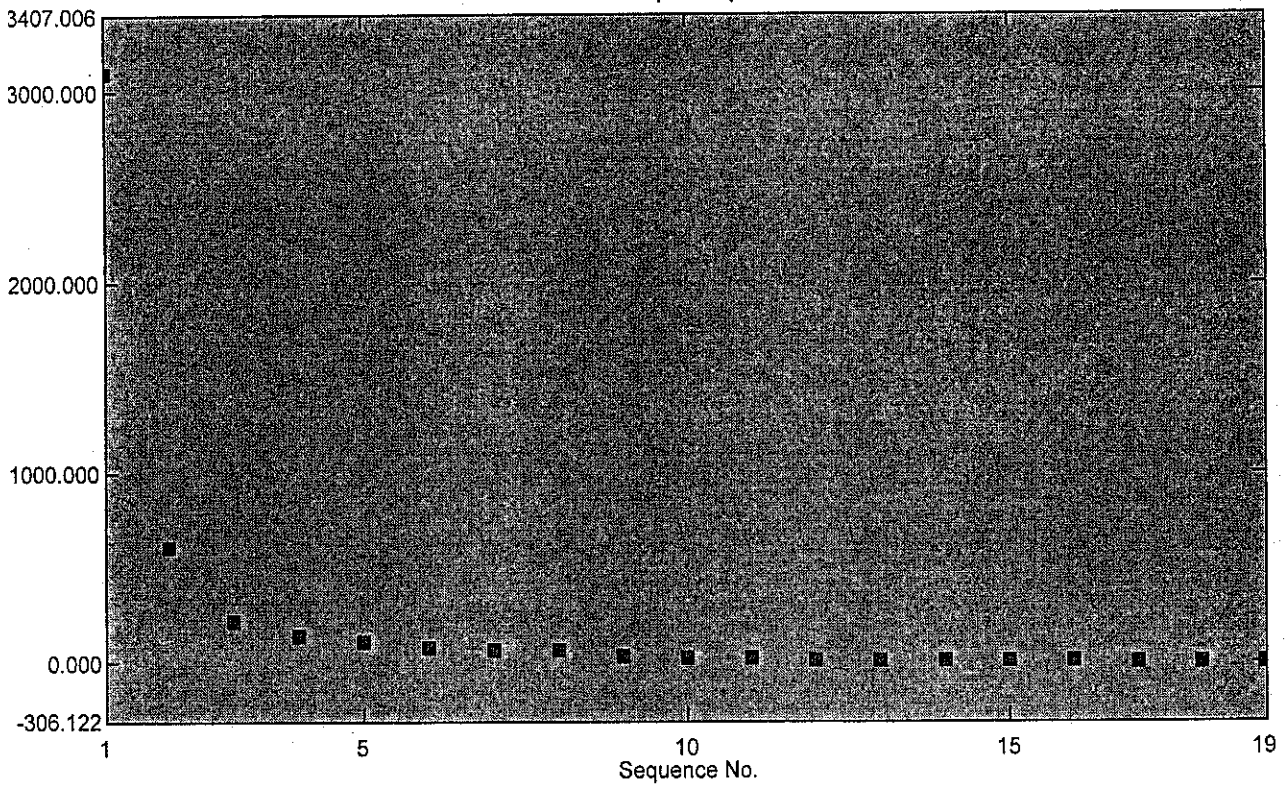
	Sample ID	Type	Ex	Conc	WL261.8	Comments
	sample19_24	Unknown		3.401	0.034	

mple Table Report

10/12/2004 09:54:08 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletolueneNaOH.pho

Sample Graph



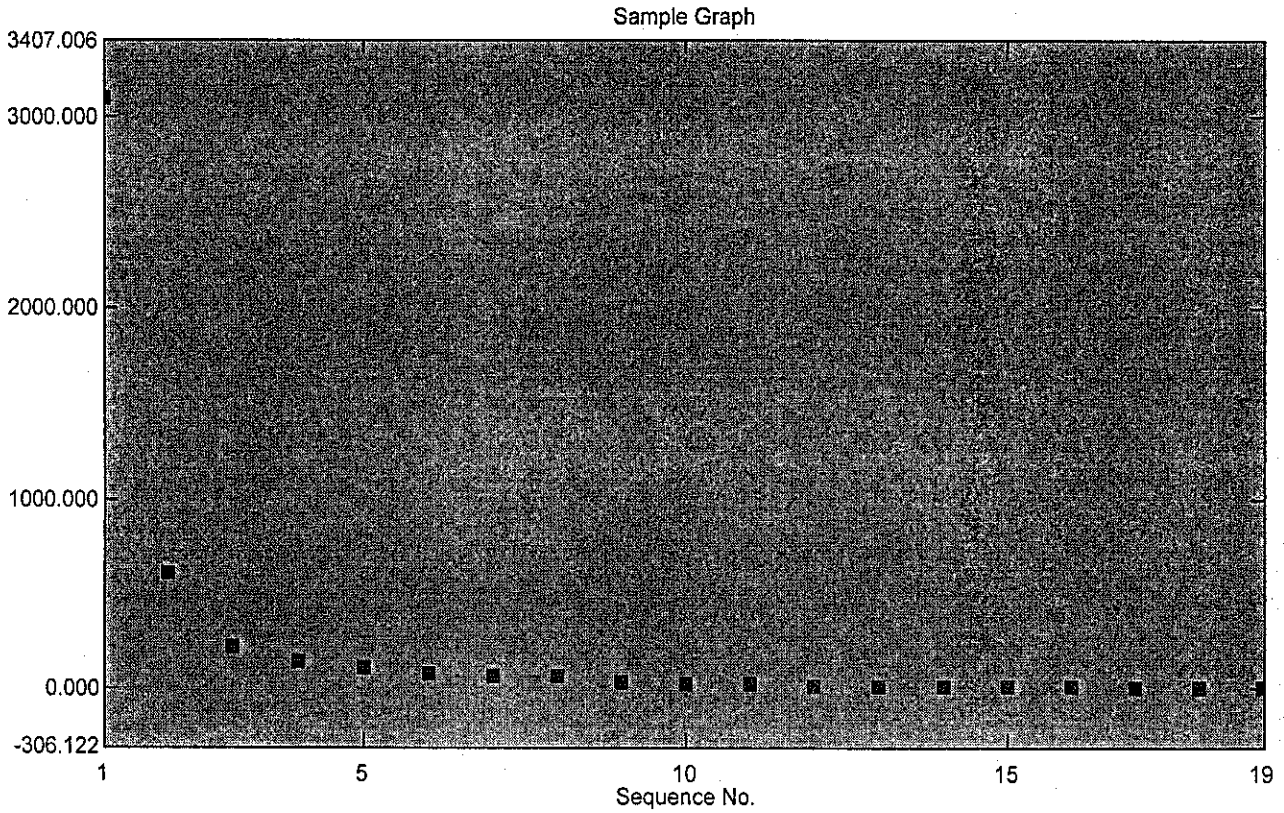
e Table

Sample ID	Type	Ex	Conc	WL261.8	Comments
sample1_0	Unknown		3097.579	5.000	
sample2_5	Unknown		613.840	1.014	
sample3_10	Unknown		211.339	0.368	
sample4_15	Unknown		137.431	0.249	
sample5_20	Unknown		104.813	0.197	
sample6_25	Unknown		74.095	0.147	
sample7_30	Unknown		63.086	0.130	
sample8_45	Unknown		63.305	0.130	
sample9_60	Unknown		27.368	0.072	
sample10_75	Unknown		21.103	0.062	
sample11_90	Unknown		15.883	0.054	
sample12_10	Unknown		10.445	0.045	
sample13_12	Unknown		10.132	0.045	
sample14_13	Unknown		10.046	0.045	
sample15_15	Unknown		9.114	0.043	
sample16_16	Unknown		9.057	0.043	
sample17_18	Unknown		3.562	0.034	
sample18_21	Unknown		3.344	0.034	

mple Table Report

10/12/2004 09:54:08 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletolueneNaOH.pho



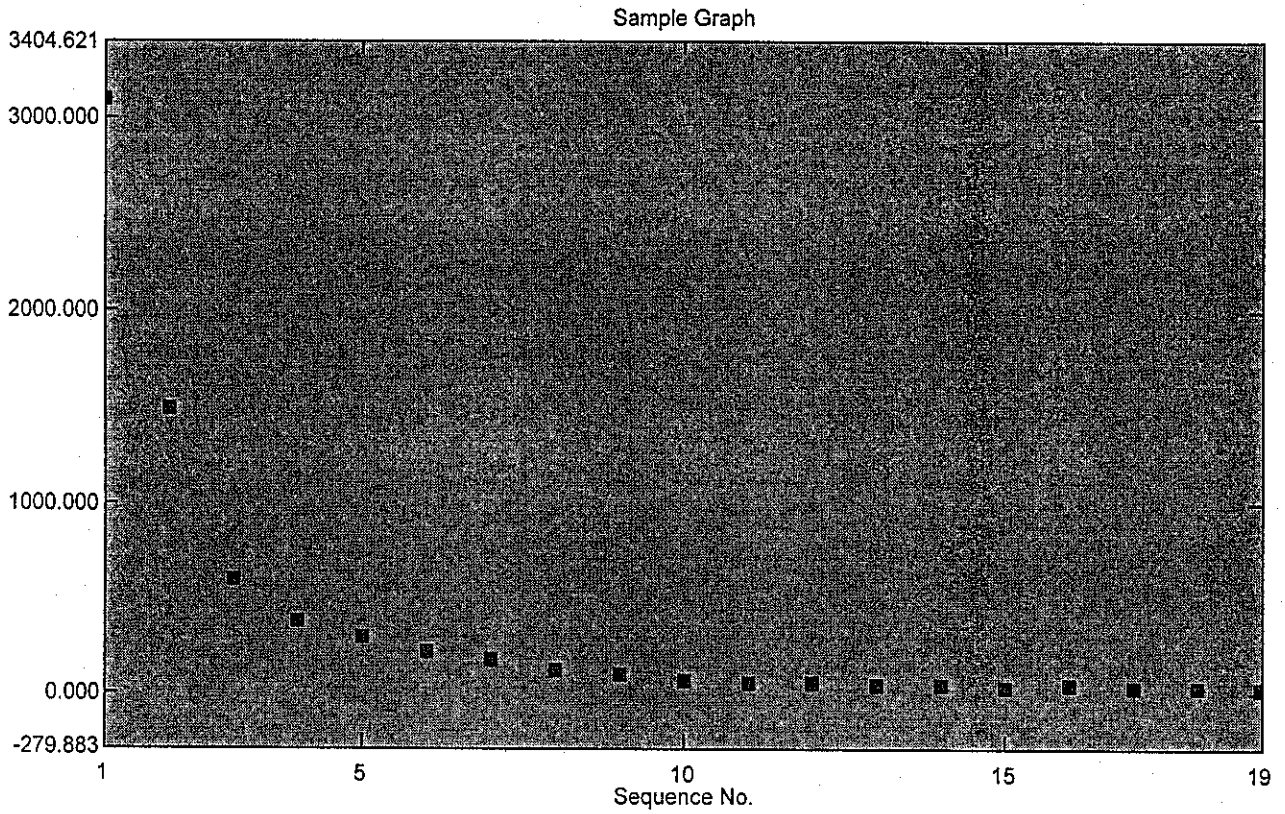
Table

Sample ID	Type	Ex	Conc	WL261.8	Comments
sample19_24	Unknown		3.306	0.034	

ımple Table Report

10/12/2004 09:46:10 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletoluene50.pho



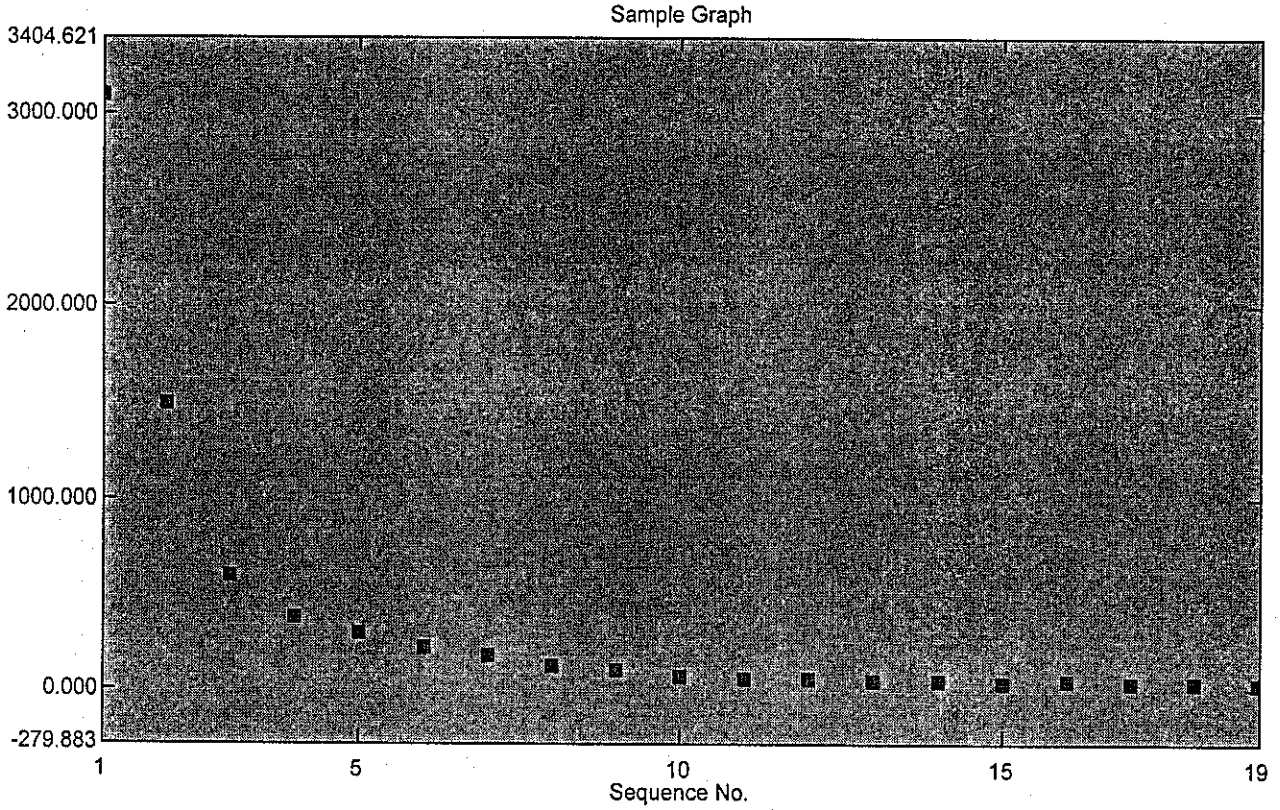
e Table

Sample ID	Type	Ex	Conc	WL261.8	Comments
sample1_0	Unknown		3097.579	5.000	
sample2_5	Unknown		1490.429	2.421	
sample3_10	Unknown		598.695	0.989	
sample4_15	Unknown		377.751	0.635	
sample5_20	Unknown		290.371	0.494	
sample6_25	Unknown		217.205	0.377	
sample7_30	Unknown		170.573	0.302	
sample8_45	Unknown		124.350	0.228	
sample9_60	Unknown		93.290	0.178	
sample10_75	Unknown		66.984	0.136	
sample11_90	Unknown		59.749	0.124	
sample12_10	Unknown		50.679	0.110	
sample13_12	Unknown		48.074	0.106	
sample14_13	Unknown		48.150	0.106	
sample15_15	Unknown		35.801	0.086	
sample16_16	Unknown		44.937	0.101	
sample17_18	Unknown		37.693	0.089	
sample18_21	Unknown		33.576	0.082	

ımple Table Report

10/12/2004 09:46:10 AM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletoluene50.pho



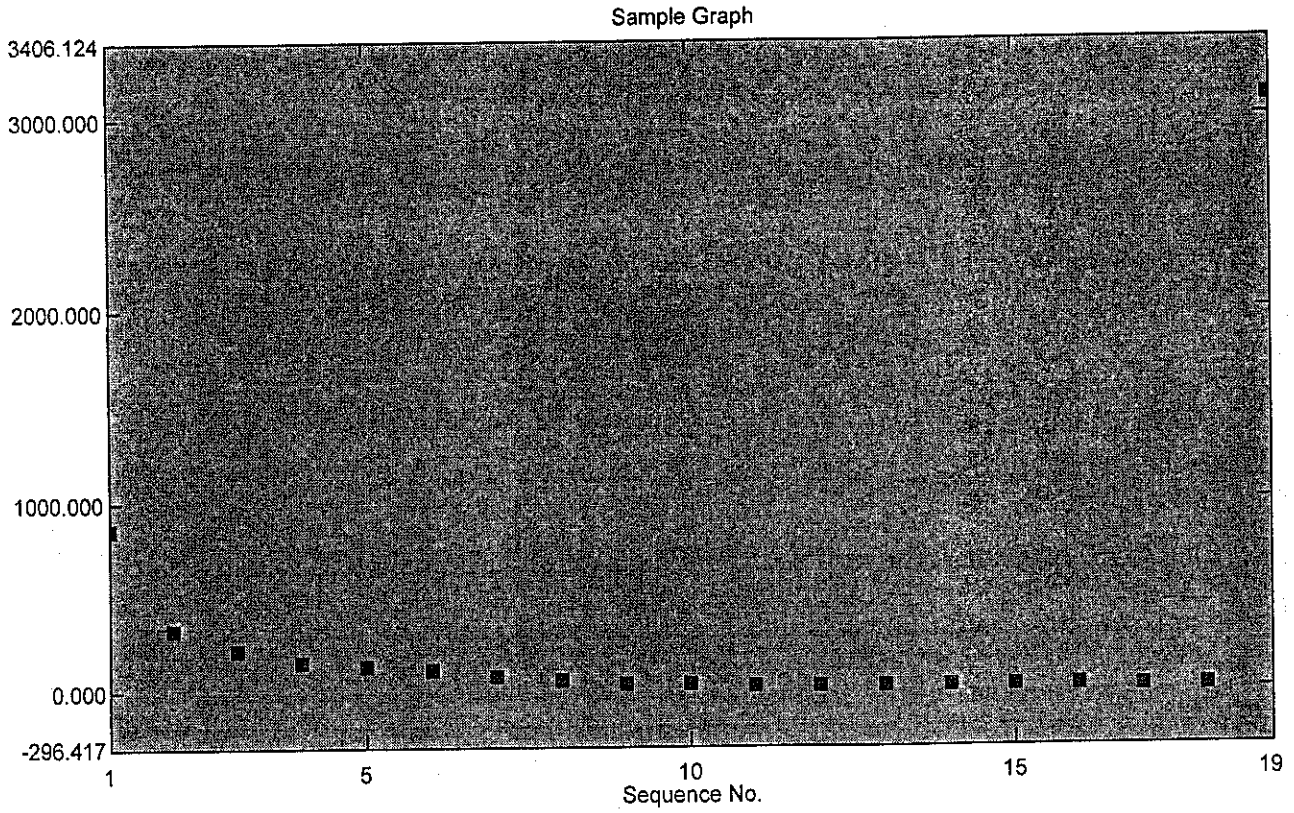
e Table

	Sample ID	Type	Ex	Conc	WL261.8	Comments
	sample19_24	Unknown		27.159	0.072	

mple Table Report

10/12/2004 04:34:27 PM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletoluene80_finalize.pho



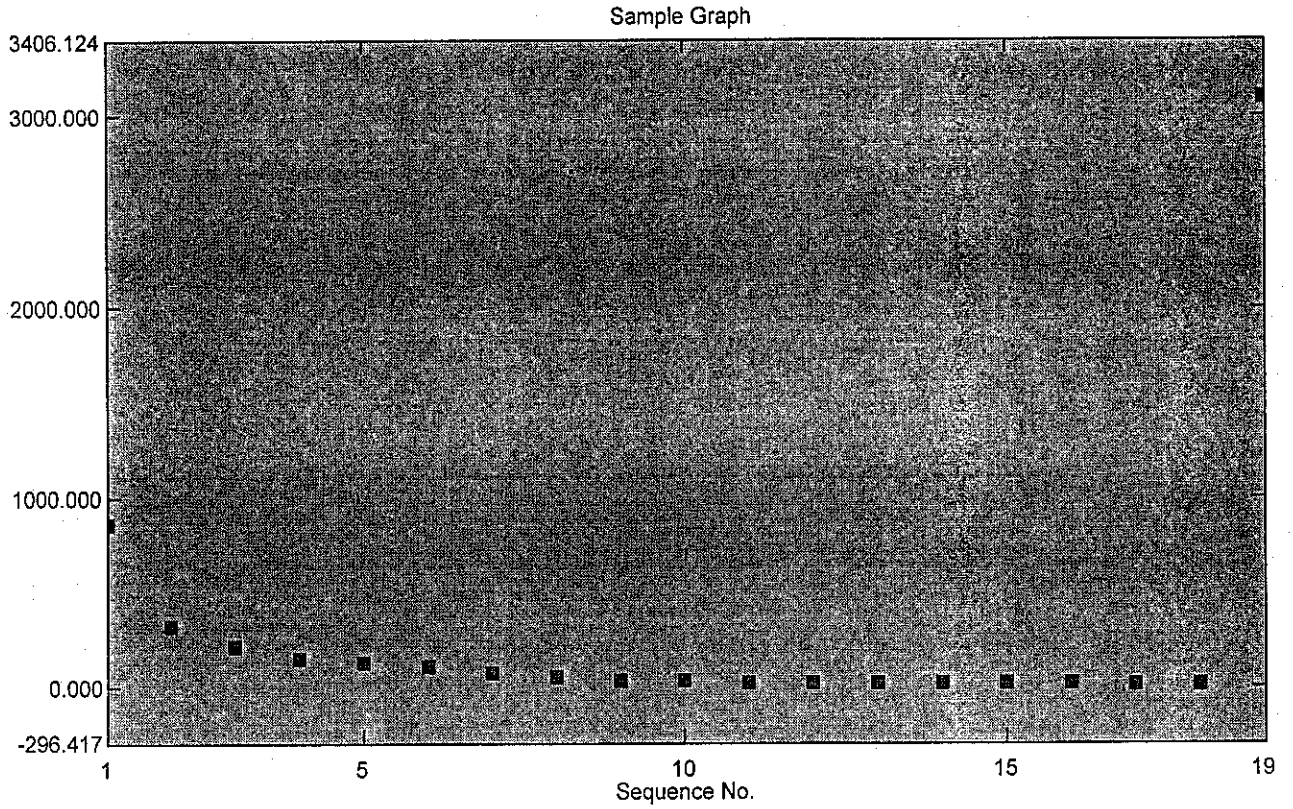
le Table

	Sample ID	Type	Ex	Conc	WL261.8	Comments
	sample2_5	Unknown		851.887	1.396	
	sample3_10	Unknown		327.154	0.553	
	sample4_15	Unknown		216.663	0.376	
	sample5_20	Unknown		143.411	0.259	
	sample6_25	Unknown		128.732	0.235	
	sample7_30	Unknown		106.847	0.200	
	sample8_45	Unknown		73.268	0.146	
	sample9_60	Unknown		45.945	0.102	
	sample10_75	Unknown		32.198	0.080	
	sample11_90	Unknown		28.281	0.074	
	sample12_10	Unknown		23.394	0.066	
	sample13_12	Unknown		21.426	0.063	
	sample14_13	Unknown		18.403	0.058	
	sample15_15	Unknown		22.519	0.065	
	sample16_17	Unknown		21.873	0.064	
	sample17_18	Unknown		20.941	0.062	
	sample18_21	Unknown		12.147	0.048	
	sample19_24	Unknown		12.128	0.048	

ımple Table Report

10/12/2004 04:34:27 PM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletoluene80_finalize.pho



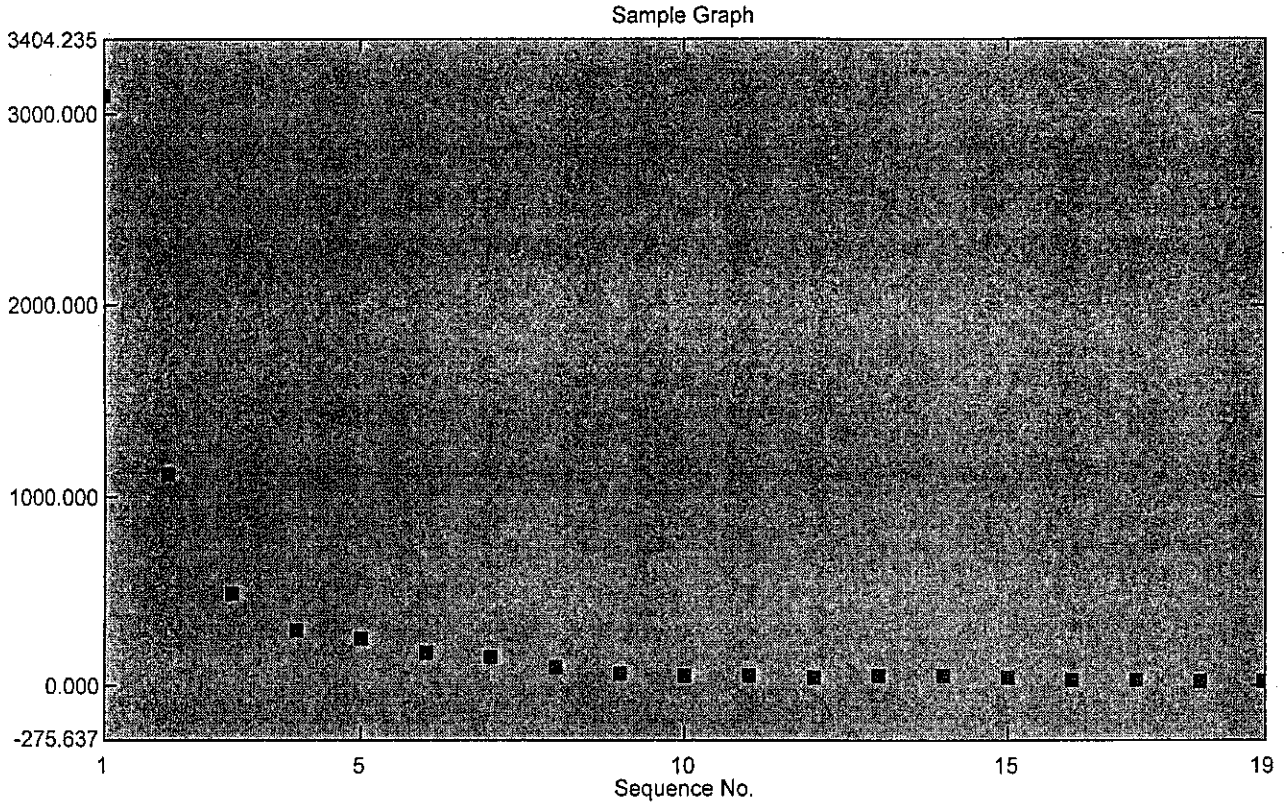
e Table

	Sample ID	Type	Ex	Conc	WL261.8	Comments
	sample1_0	Unknown		3097.579	5.000	

mple Table Report

10/12/2004 04:36:07 PM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletoluene120_finalize.pho



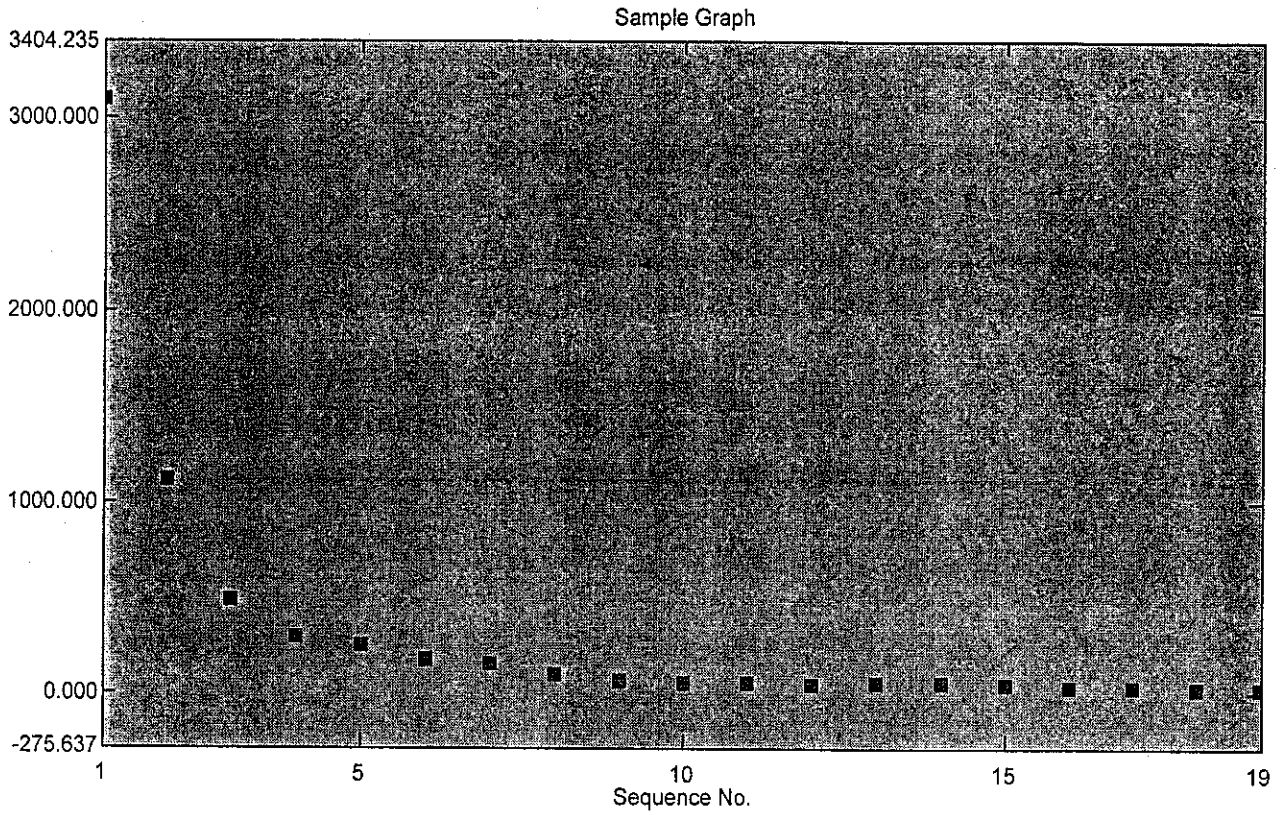
Table

Sample ID	Type	Ex	Conc	WL261.8	Comments
sample1_0	Unknown		3097.579	5.000	
sample2_5	Unknown		1120.937	1.827	
sample3_10	Unknown		485.703	0.808	
sample4_15	Unknown		290.970	0.495	
sample5_20	Unknown		250.109	0.430	
sample6_25	Unknown		180.917	0.319	
sample7_30	Unknown		151.711	0.272	
sample8_45	Unknown		96.960	0.184	
sample9_60	Unknown		66.081	0.134	
sample10_75	Unknown		59.721	0.124	
sample11_90	Unknown		55.176	0.117	
sample12_10	Unknown		48.540	0.106	
sample13_12	Unknown		54.900	0.117	
sample14_13	Unknown		54.178	0.115	
sample15_15	Unknown		45.973	0.102	
sample16_16	Unknown		36.866	0.088	
sample17_18	Unknown		38.624	0.090	
sample18_21	Unknown		31.123	0.078	

mple Table Report

10/12/2004 04:36:07 PM

Name: C:\Program Files\Shimadzu\UVProbe\Data\FYPjan2004\Marina\sampletoluene120_finalize.pho



Table

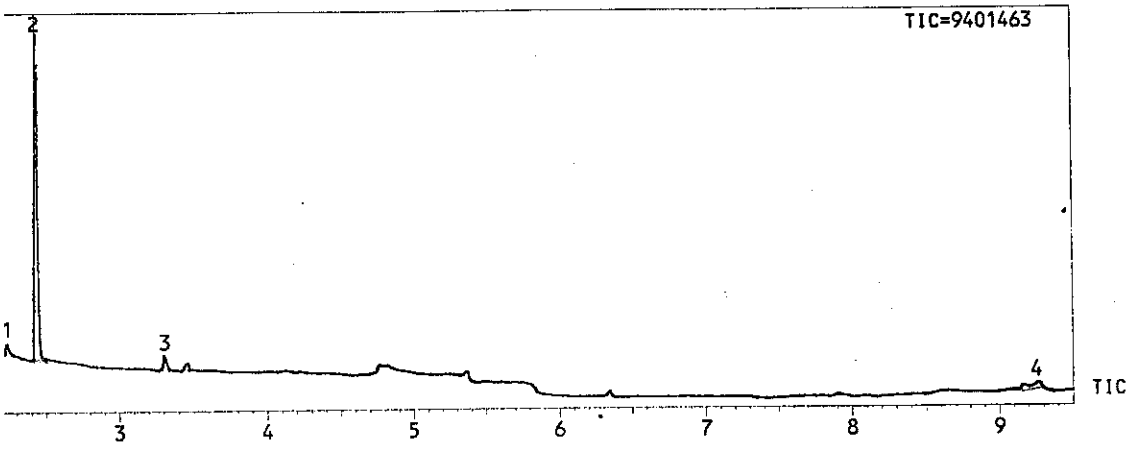
	Sample ID	Type	Ex	Conc	WL261.8	Comments
	sample19_24	Unknown		31.019	0.078	

Appendix D: Standard Calibration Curve of Toluene

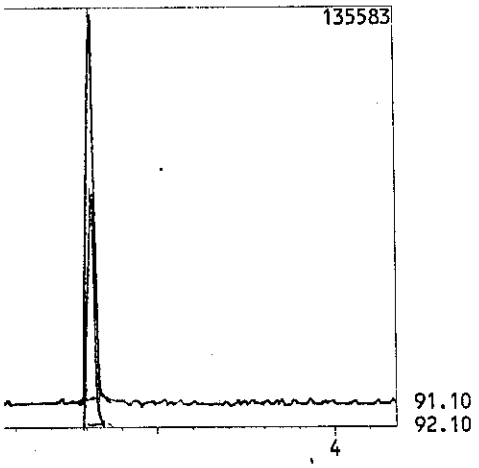
CLASS-5000 *** Report No. = 1 Data : MARINA2.D01 04/10/12 08:38:57

ɔle : std_toluene1ppm
: toluene1ppm
: Standard
ɔod File Name : MARINA2.MET

Chromatogram ***



Quantitation ***



ID : 1 M/Z : 91.10
Type : Target
Name : Toluene

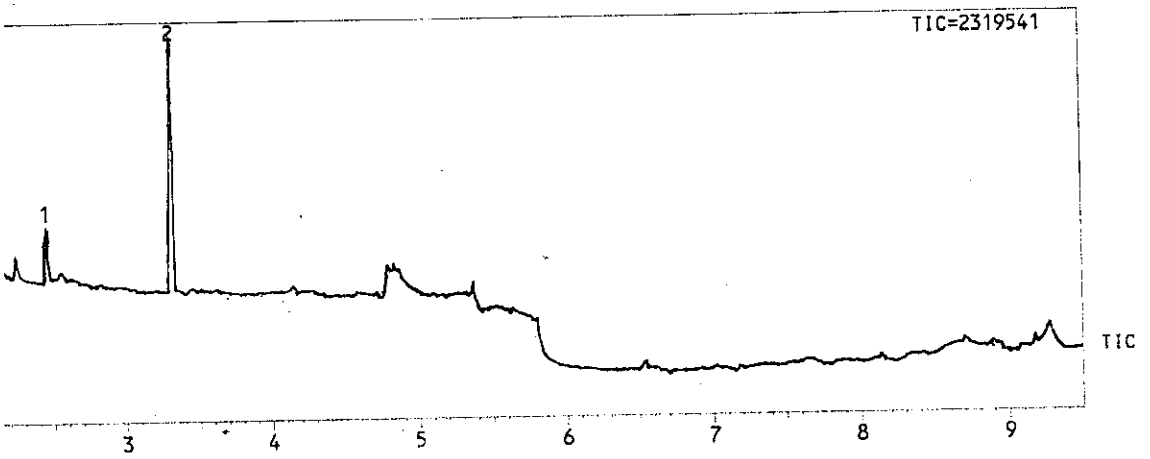
Time : 3.314
Area : 169918

	M/Z	Area	%Rel.Int.to Target
1	92.10	106418	63

CLASS-5000 *** Report No. = 2 Data : MARINA2.D03 04/10/12 09:40:28

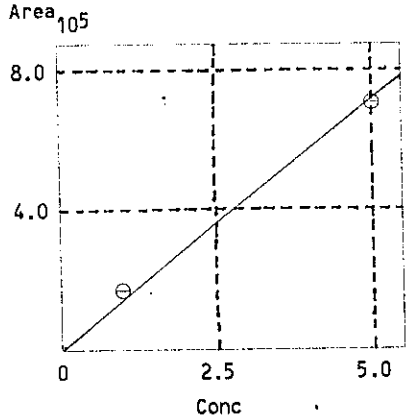
ple : std_toluene5ppm
: toluene5ppm
e : Standard
hod File Name : MARINA2.MET

Chromatogram ***



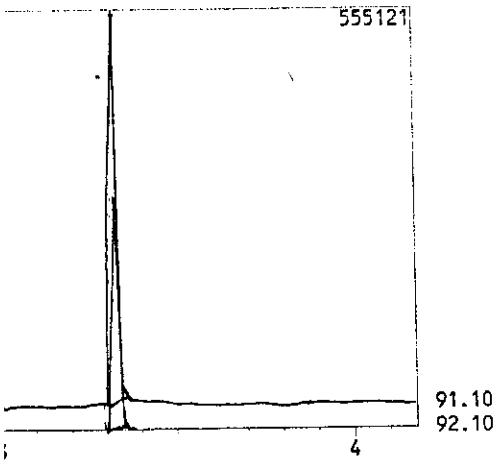
* Calibration Curve ***

ID # 1 M/Z : 91.10 Name : Toluene
Area = 141556 * (Conc.) r2 = 1.000000



	Conc.( )	Area
1	1.000	169918
2	5.000	702108

** Quantitation ***



ID : 1 M/Z : 91.10
Type : Target
Name : Toluene

Time : 3.322
Area : 702109

	M/Z	Area	%Rel.Int.to Target
1	92.10	422022	60